# STUDIES IN THE MESOBENZANTHRONE SERIES

BY

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Doctor of Philosophy

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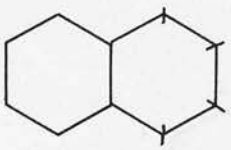
# I N D E X

## PREFACE

Throughout this Thesis, completely aromatic nuclei are represented by totally unadorned drawings. The correspondingly saturated structure is demonstrated by the presence of cross-hatching. Thus, the formula employed for tetralin on this basis is that shown below.



Tetralin (1:2:3:4-tetrahydro-naphthalene)

In the Experimental Sections, all melting point determinations below 350°C were performed initially on a Kofler hot-stage microscope. Melting points above this figure were obtained by means of a Townson-Mercer apparatus.

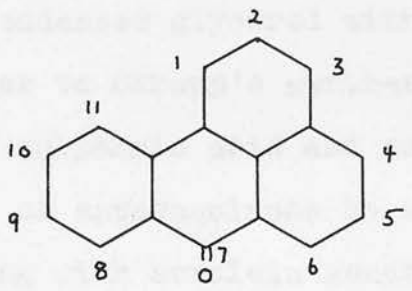
The alumina utilised in chromatographic separations was of a grade supplied by Spence.

Ultraviolet spectroscopic data were obtained with the aid of a Unicam SP 500 ultraviolet absorption spectrophotometer, whilst fluorescence studies were effected in the beam of a Hanovia ultraviolet lamp.

All analyses were performed by Drs. Weiler and Strauss, of Oxford.

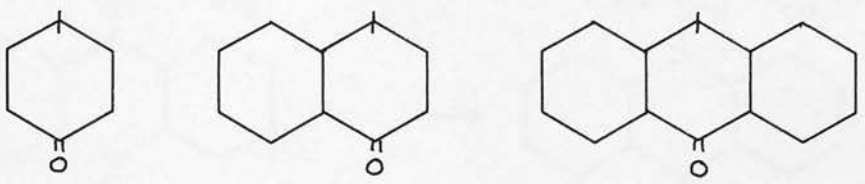
## GENERAL INTRODUCTION

As its name infers, the aromatic ketone mesobenzanthrone consists structurally of a benzene ring fused to the 1:9 positions of the anthrone molecule. Under the present Chemical Abstracts nomenclature, it appears as 7-(H)-Benz (d,e) anthracene-7-one, and the currently accepted numbering of the nucleus, which will be used throughout the Thesis, is shown.




I

Mesobenzanthrone, a bright yellow crystalline solid, may be regarded as a member of the series commencing with the keto form of phenol (II), the keto form of naphthol (III), and anthrone (IV).



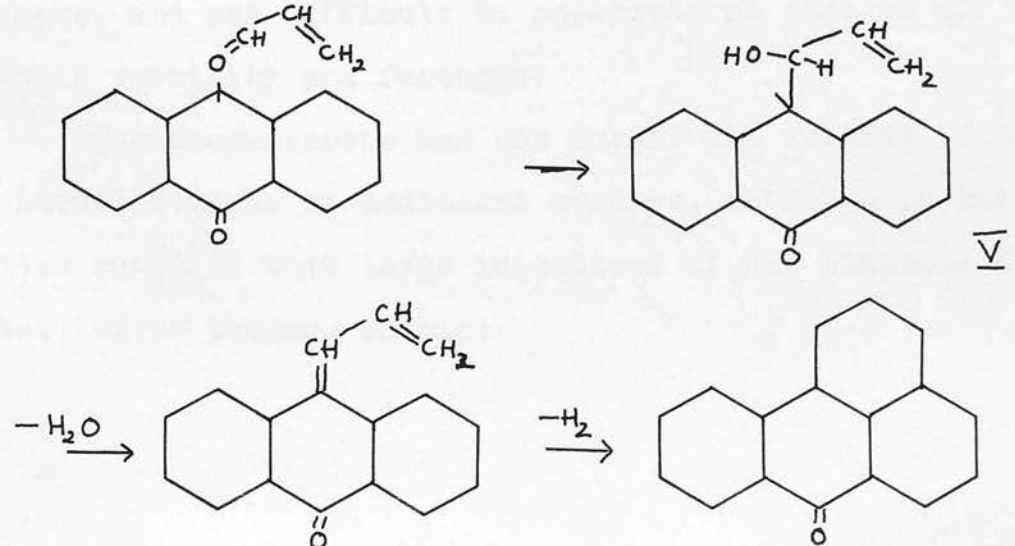

II III IV

Each member of the series possesses one fused benzene

ring in excess of its direct predecessor, and as a consequence of this, the ketonic tautomer tends to predominate as the series ascends. Thus (II) and (III) exist entirely as enols, the two forms of (IV), anthrone and anthranol, are easily interconvertible, and (I) may only be formulated as a ketone, no tautomerism being possible in this case.

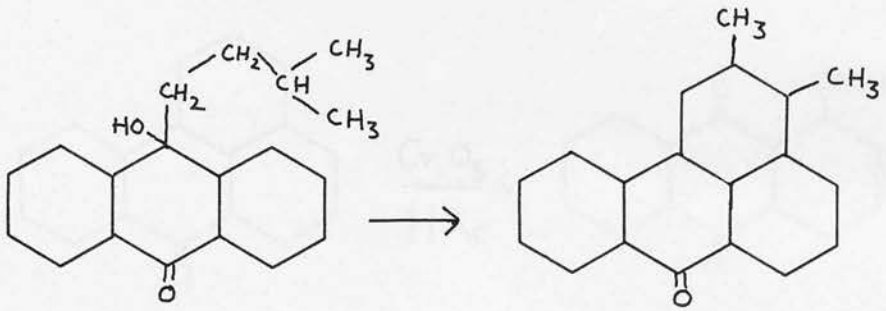
A resemblance between the structure of mesobenzanthrone and that of anthraquinone is at once apparent. The preparation of the former was first achieved by Bally[1], who condensed glycerol with anthraquinone, in a fashion similar to Skraup's synthesis of quinoline. The presence of sulphuric acid and copper effected the prior reduction of anthraquinone to anthrone, this latter condensing with acrolein generated in situ by dehydration of the glycerol.

The mechanism of this reaction has been conclusively established[2] as a carbonyl-methylene condensation to yield the intermediate (V). This dehydrates to form the allylidene anthrone, which undergoes cyclodehydrogenation to mesobenzanthrone.



Bally's synthesis has found great application in the preparation of substituted mesobenzanthrones, and further reference will later be made to this and other syntheses.

Although mesobenzanthrone was first synthesised in 1905, Liebermann[3], some twenty years previously, cyclised meso-isoamyl oxanthranol (VI) with sulphuric acid, to obtain what was subsequently[4] proved to be 2,3-dimethyl-mesobenzanthrone (VII), migration of a methyl group having occurred.




VI VII

Commercially, the importance of mesobenzanthrone is in the dyestuffs industry, where many derivations, notably dibenzanthrones, form a series of vat dyes, which have been on large scale production for many years, and are difficult to supersede on account of their stability and fastness.

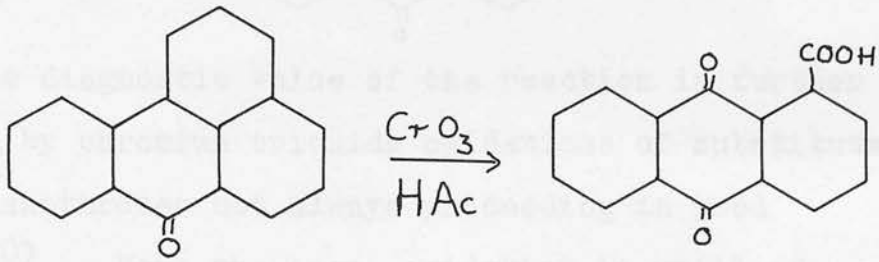
Mesobenzanthrone has not formed the subject of any pharmacological or medicinal studies, although it has been noted[5] that large injections of the compound do not induce tumours in mice.

## Properties of the Mesobenzanthrone nucleus

### 1. Oxidation and Reduction

Although mesobenzanthrone and its derivatives are normally stable substances, it is possible to rupture the parent molecule fairly easily.

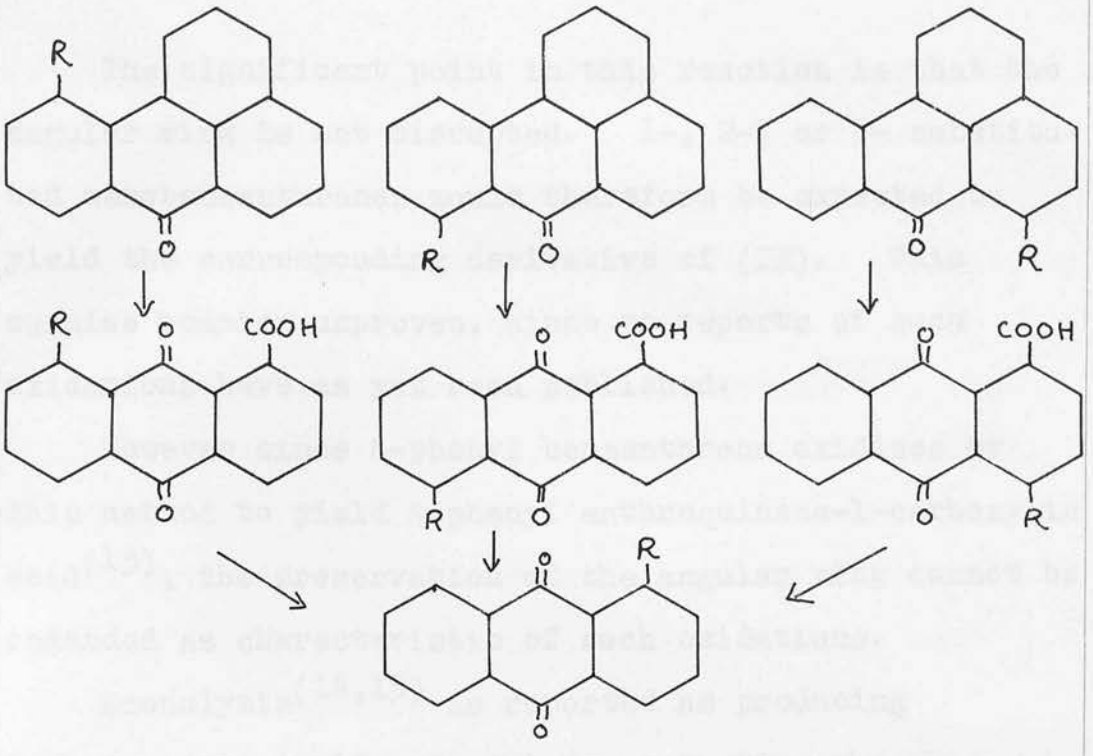
Heating with chromium trioxide in acetic acid causes cleavage of the angular ring, and anthraquinone-1-carboxylic acid (VIII) may be isolated in good yield from the unsubstituted ketone[6].




VIII

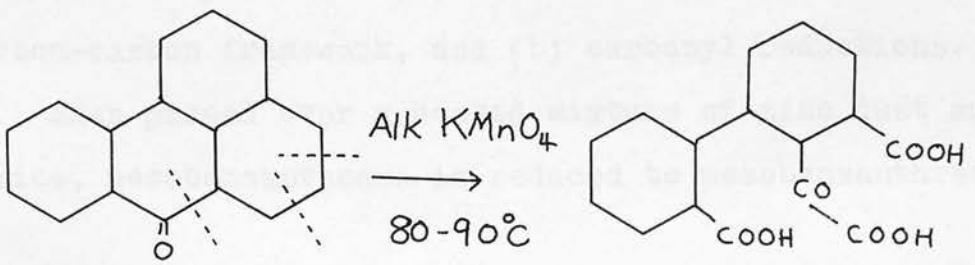
In substituted mesobenzanthrones, the substituent is usually unaffected by oxidation, providing it is in the anthraquinone part of the molecule[7,8,9], and decarboxylation of the resulting anthraquinone carboxylic acid gives a substituted anthraquinone.

It will be noted that the product obtained from the decarboxylation of the acids derived from oxidation of 6-, 8-, and 11- substituted mesobenzanthrones is, in each case, a 1- substituted anthraquinone. Hence, distinction between such isomers is not possible by this approach.




The diagnostic value of the reaction is further limited by chromium trioxide oxidations of substituted mesobenzanthrones not always proceeding in good yield[10]. None the less, oxidation is still of fundamental value in orientation studies.

Less extensively investigated is the oxidation of mesobenzanthrone with alkaline potassium permanganate[11,12]. In this case, some anthraquinone-1-carboxylic acid is formed, but the main product is 2',3-dicarboxy-biphenyl-2-glyoxylic acid (IX), formed by cleavage of the parent molecule in the positions indicated.

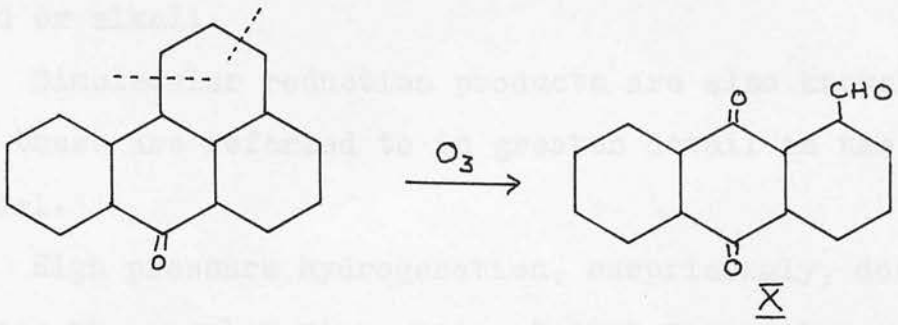



IX

The significant point in this reaction is that the angular ring is not disrupted. 1-, 2-, or 3- substituted mesobenzanthrones would therefore be expected to yield the corresponding derivative of (IX). This surmise remains unproven, since no reports of such oxidations have as yet been published.

However since 6-phenyl benzanthrone oxidises by this method to yield 4-phenyl anthraquinone-1-carboxylic acid[13], the preservation of the angular ring cannot be regarded as characteristic of such oxidations.

Ozonolysis[14,15] is reported as producing anthraquinone-1-aldehyde (X) demonstrating the reactivity of this part of the molecule.




X

Further evidence of the site of reactivity is shown by reduction studies.

The reduction of mesobenzanthrone may be considered from two viewpoints:- (a) The reduction of the nuclear carbon-carbon framework, and (b) carbonyl reductions.

When passed over a heated mixture of zinc dust and pumice, mesobenzanthrone is reduced to mesobenzanthrene

(XI). A dihydromesobenzanthrene (XII) results from reduction with red phosphorus and iodine, whereas dihydromesobenzanthrone (XIII) is reported to be formed by reduction with zinc dust and alkali, with ammonia, or with alkaline sodium hyposulphite[16].

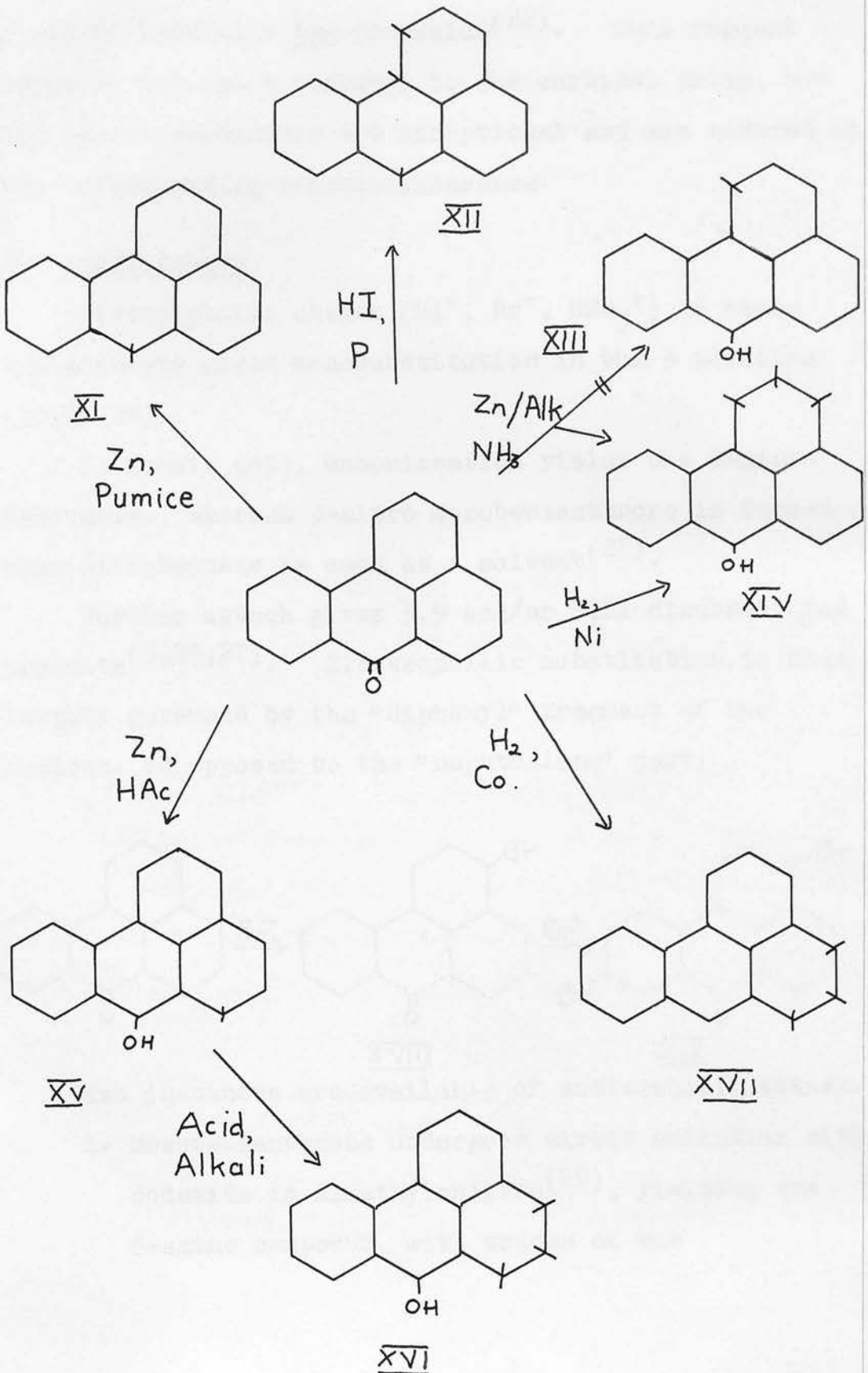
On repetition of this latter reduction[17], the product was shown to be 1,9,tri-methylene 10-anthranol (XIV), also formed by catalytic hydrogenation of meso-benzanthrone in the presence of nickel salts[18]. (XIV) was further hydrogenated to 1,9 trimethylene 5;6;7;8-tetrahydroanthranol.

By reduction with zinc dust and acetic acid, Clar[19] obtained another dihydromesobenzanthrone (XV), which disproportionated to (XVI) and mesobenzanthrone in acid or alkali.

Bimolecular reduction products are also known[20], and these are referred to in greater detail in the sequel.

High pressure hydrogenation, surprisingly, does not attack the angular ring, and, at high temperatures in the presence of a cobalt catalyst, 1,10 trimethylene phenanthrene (XVII) is isolated[21].

Reduction products of Mesobenzanthrone



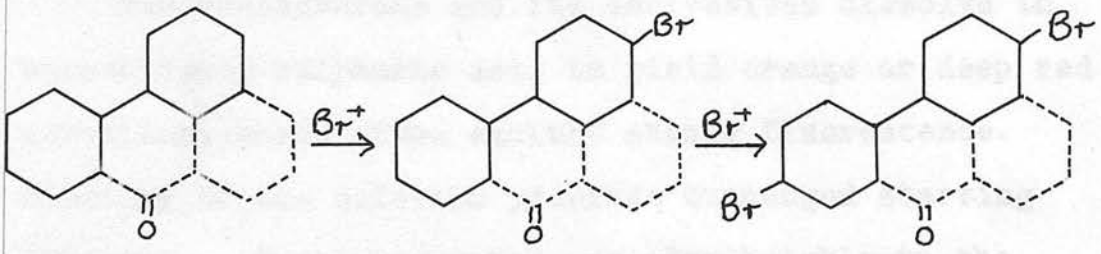
Exclusive reduction of the carbonyl group in the parent and substituted compounds may be effected in good yield by aluminium iso-propoxide[22]. This reagent normally reduces a carbonyl to the carbinol group, but the mesobenzanthrones are exceptional and are reduced to the corresponding mesobenzanthrenes.

2. Substitution

Electrophilic attack ($Cl^+$, $Br^+$, $HSO_3^+$) of mesobenzanthrone gives monosubstitution in the 3 position (10,23,24).

In acetic acid, mononitration yields the 2-nitro derivative, whereas 3-nitro mesobenzanthrone is formed when nitrobenzene is used as a solvent[25].

Further attack gives 3,9 and/or 3,11 disubstituted products[9,26,27]. Electrophilic substitution is thus largely governed by the "diphenyl" fragment of the nucleus, as opposed to the "naphthalene" part.



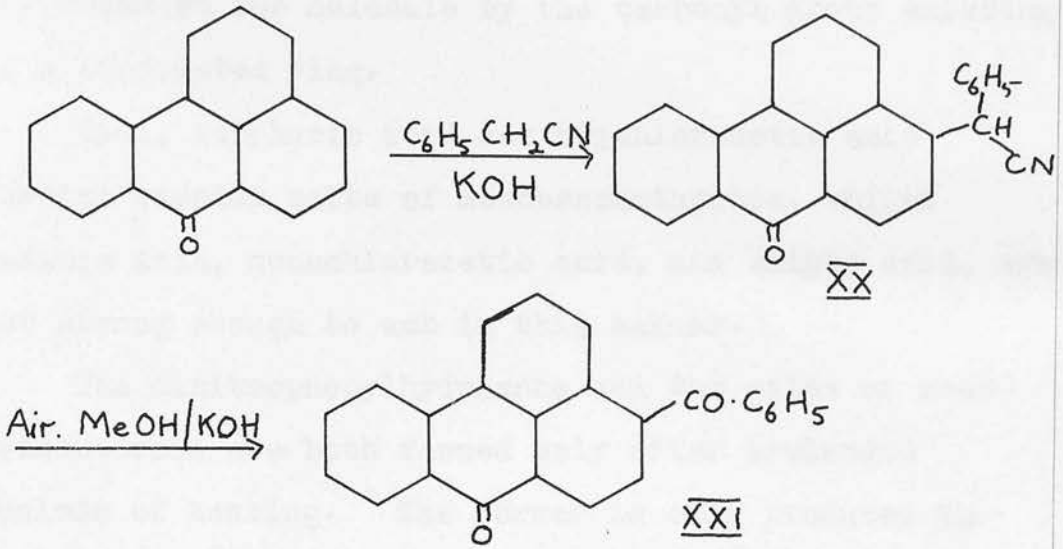

XVIII XIX

Two instances are available of nucleophilic attack.

1. Mesobenzanthrone undergoes direct amination with sodamide in dimethylaniline[28], yielding the 6-amino compound, with traces of the

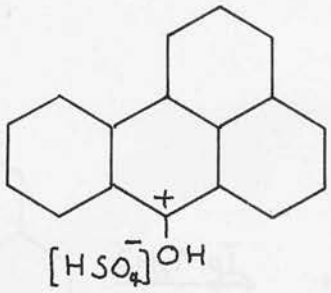
4-substituted product.

2. Molecules containing a reactive methylene group (e.g. acetone, acetophenone, benzyl cyanide) may be condensed with mesobenzanthrone in an alkaline medium[29,30]. With benzyl cyanide, 4-$\alpha$-cyanobenzyl-mesobenzanthrone (XX) results, and this readily undergoes oxidative hydrolysis to 4-benzoyl-mesobenzanthrone (XXI).




3. Carbonyl properties of Mesobenzanthrone

Mesobenzanthrone and its derivatives dissolve in concentrated sulphuric acid to yield orange or deep red solutions, which often exhibit strong fluorescence. Dilution of the solution provides unchanged starting material. Such properties are attributable to the formation of an oxonium salt, whose probable structure is as shown.

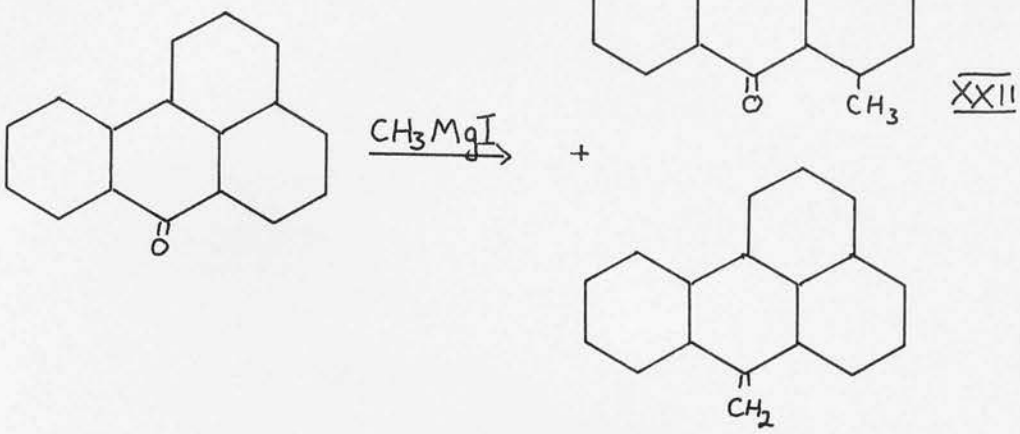



Further, the isolation of certain complex salts of mesobenzanthrone[31] is indicative of some weak basicity conferred on the molecule by the carbonyl group existing in a conjugated ring.

Thus, sulphuric acid and trichloracetic acid furnish oxonium salts of mesobenzanthrones, whilst benzoic acid, monochloracetic acid, and adipic acid, are not strong enough to act in this manner.

The dinitrophenylhydrazone and the oxime of mesobenzanthrone are both formed only after prolonged periods of heating. The former is only produced in poor yield, whereas the oximation occurs in good yield[22].

Attack by Grignard reagents occurs by means of a 1:4 addition, the product being a 6-substituted benzanthrone[10,23]. An exception to this is reported[23], where methylmagnesium iodide reacts to give a mixture of 6-methyl mesobenzanthrone (XXII) and 7-methylene-mesobenzanthrene (XXIII).




XXII

XXIII

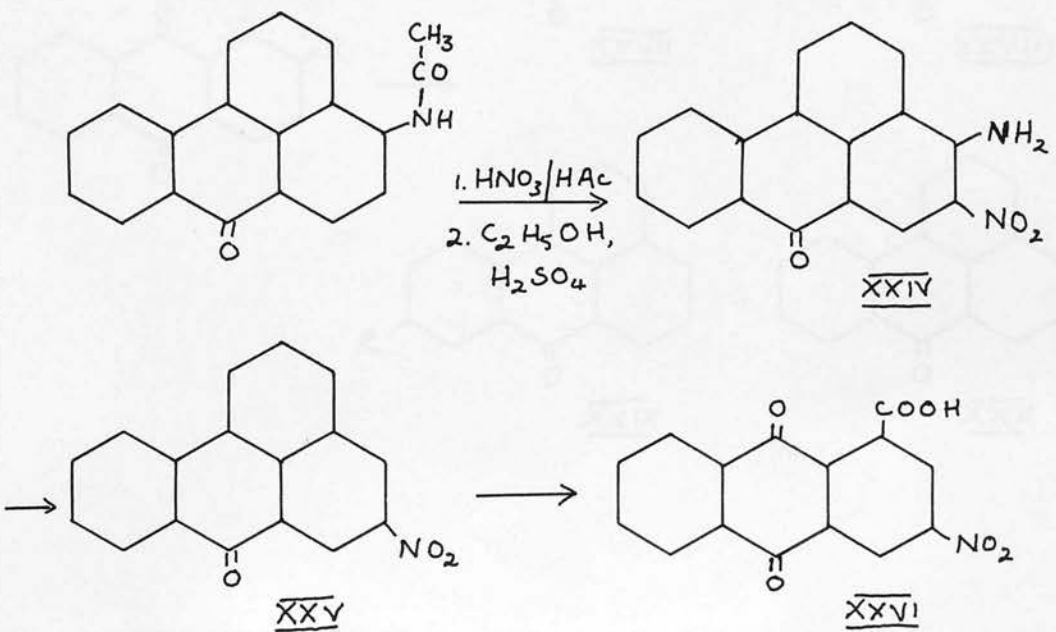
## 8-substituted Mesobenzanthrones

### Discussion

From the foregoing, it is clear that suitable treatment of the unsubstituted ketone will result in the formation of 2-, 3-, 4-, 6-, and 9-substituted mesobenzanthrones.

Malhotra et al.[32] have devised a method for the synthesis of 5-substituted isomers, whereby 4-acetylaminomesobenzanthrone (prepared in two stages from the 4-hydroxy-compound) is mononitrated. Deacetylation furnished a nitroaminomesobenzanthrone, (XXIV), which, when reduced to the diamine, formed quinoxalines and imidazoles, thereby indicating that ortho nitration had occurred.

Diazotisation of the nitroamine removed the amino group, with the formation of 5-nitromesobenzanthrone, (XXV), conclusively orientated by oxidation to 3-nitroanthraquinone-1-carboxylic acid (XXVI).

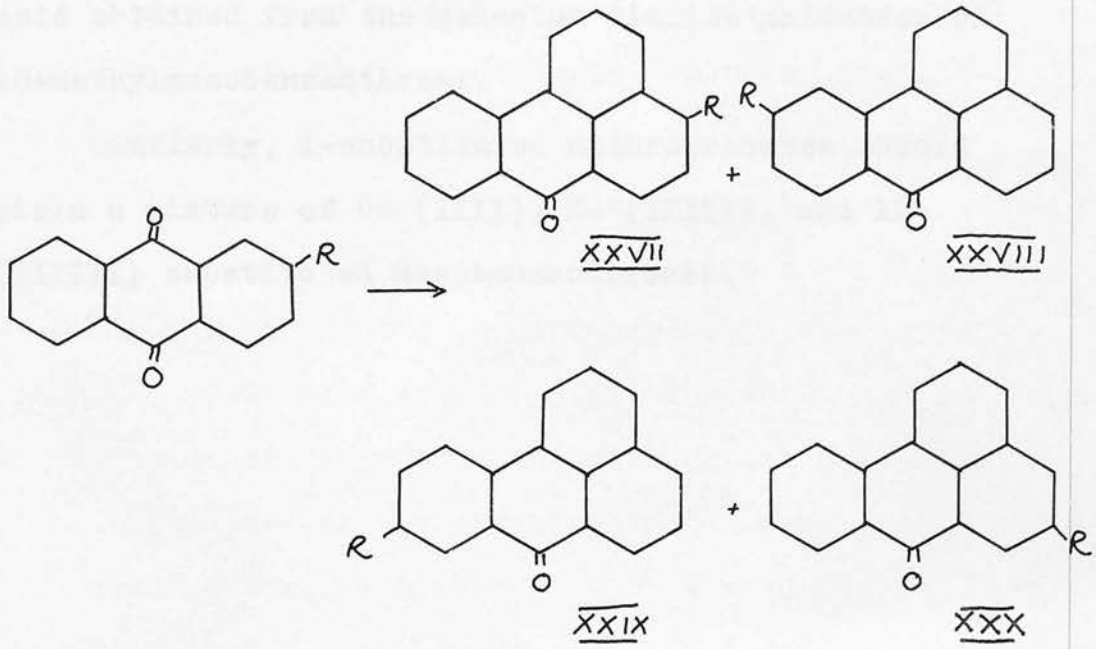


The 1-, 8-, 10-, and 11-substituted compounds cannot be prepared directly from the parent substance. In order to achieve the unequivocal synthesis of these compounds it is therefore necessary to utilise derivatives of intermediates that are employed in the preparation of mesobenzanthrone.

Unexpected difficulties have been encountered only in the case of the 8-isomers, and this section deals chiefly with attempts to prepare reasonable quantities of such compounds.

By starting with substituted anthraquinones and anthrones, Bally's synthesis may be extended to include the preparation of substituted mesobenzanthrones.

In theory, 2-substituted anthraquinones could furnish a mixture of 4-, 5-, 9-, and 10-substituted mesobenzanthrones, (XXVII - XXX).



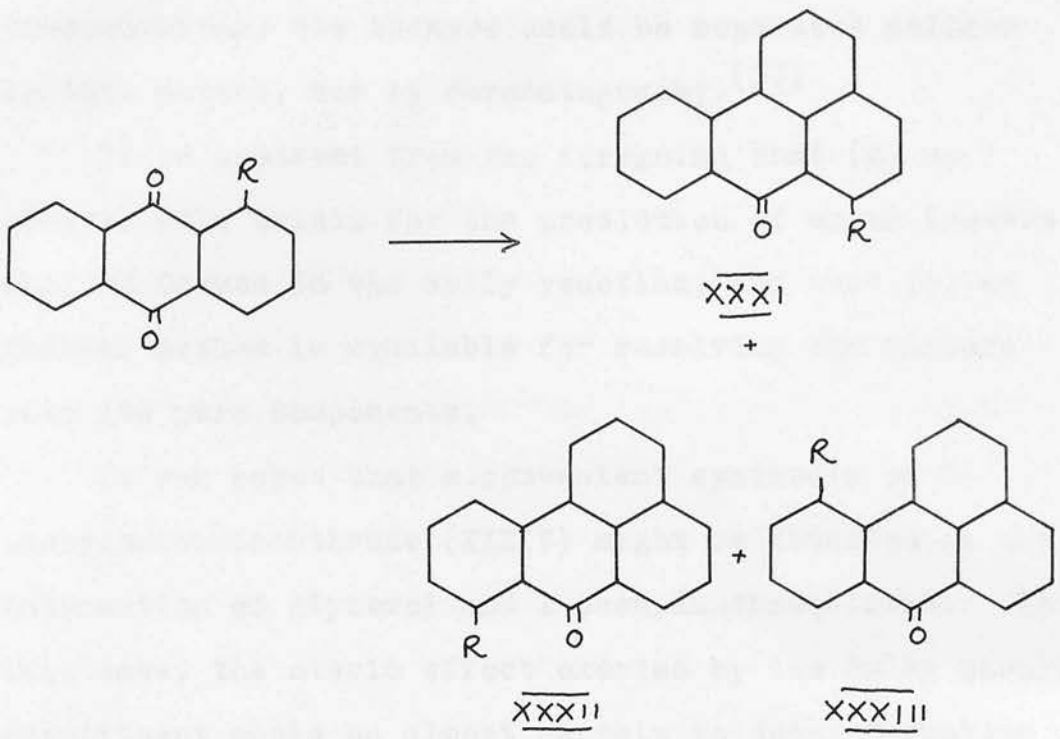
Pandit, Tilak, and Venkataraman[33] have shown that 2-chloroanthraquinone yields, as the main product, 4-chloro-mesobenzanthrone (XXVII, R = Cl) which was identified by oxidative degradation.

The 9- (XXIX, R = Cl), and 10- (XXVIII, R = Cl) isomers were also isolated in smaller quantities, but no formation of 5-chloromesobenzanthrone was observed by these workers.

Again, Copp and Simonsen,[34] performing a similar reaction with anthraquinone-2-carboxylic acid, only isolated the 9-, and 10-carboxylic acids, separated by chromatography of the ethyl esters. The 9-acid was orientated by the Schmidt reaction, the resulting aminomesobenzanthrone being converted to the known 9-chloromesobenzanthrone by a Sandmeyer reaction.

The 10- acid was orientated by a comparison of the acid obtained from the selenium dioxide oxidation of 10-methylmesobenzanthrone.

Similarly, 1-substituted anthraquinones should yield a mixture of 6- (XXXI), 8- (XXXII), and 11- (XXXIII) substituted mesobenzanthrones.




Maki and Kikuti[35] claim to have isolated all three isomers from 1-chloroanthraquinone, but oxidative degradation was performed only on the 11-chloromesobenzanthrone.

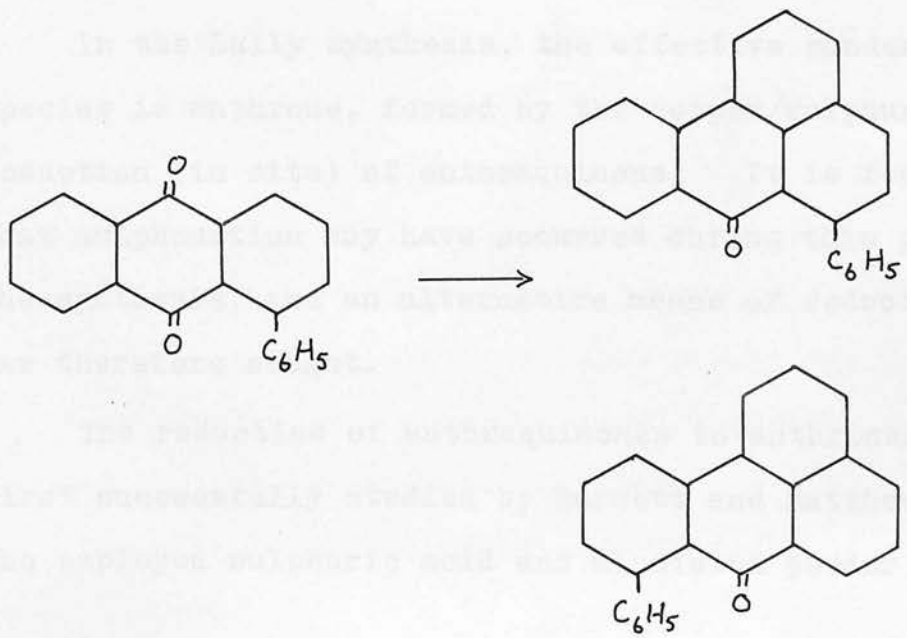
Copp and Simonsen[34] demonstrated that, whilst anthraquinone-1-carboxylic acid provided no identifiable product, due presumably to lactonisation, the amide yielded a mixture of the 6- (XXXI, R = COOH) and 8- (XXXII, R = COOH) acids, separable by ester chromatography.

The mixture of chloromesobenzanthrones, obtained from treatment of 1-chloro-9-anthrone with glycerol and sulphuric acid[36] was separated into 6- and 8-chloro-

mesobenzanthrones by means of the different solubility of these compounds in alcohol. For the corresponding bromoanthrone, the isomers could be separated neither by this method, nor by chromatography.(37)

It is apparent from the foregoing that (a) no general rule exists for the prediction of which isomers will be formed in the Bally reaction, and that (b) no general method is available for resolving the mixture into its pure components.

It was hoped that a convenient synthesis of 8-phenylmesobenzanthrone (XXXIV) might be obtained by the interaction of glycerol and 1-phenylanthraquinone. In this case, the steric effect exerted by the bulky phenyl substituent would be almost certain to debar formation of the 11-phenyl isomer, and the separation of a possible mixture of the 6- and 8- compounds could be attempted either by crystallisation or by chromatography.




XXXIV

The product from this reaction, a black granular solid, was readily water soluble, a property to be expected of sulphonated material. Proof that such an undesirable side reaction had, in fact, taken place was forthcoming from a Lassaigne fusion test, which demonstrated the presence of sulphur.

Unsuccessful attempts to minimise sulphonation, by reducing the condensation time and temperature were made, but in no case was any water insoluble material isolated.

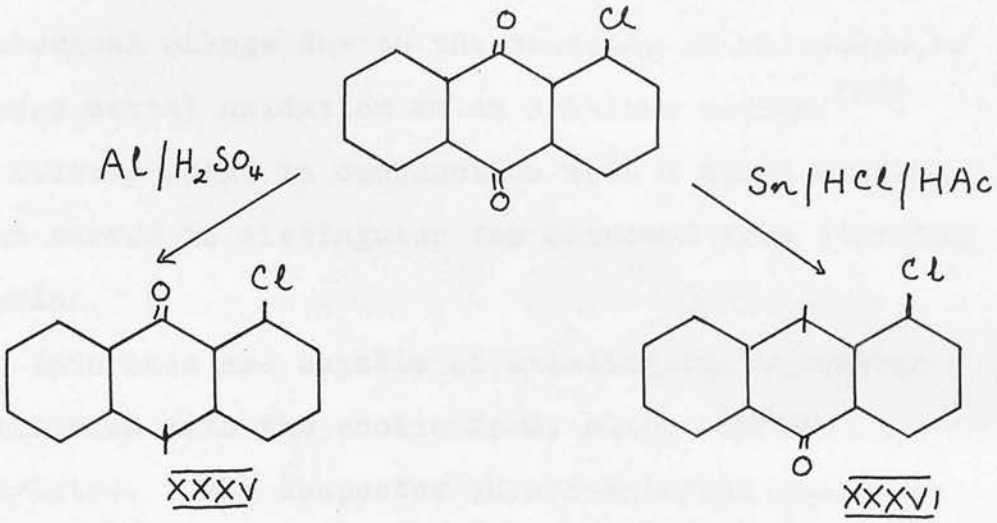
Normally, sulphonation is not a hazard greatly encountered in the Bally synthesis, yet it has been noted as occurring in the ring closure of 1-(2'-carboxy-phenyl)-2-methylnaphthalene, which is better cyclised by a Friedel Crafts method.[38]

Heating with 50-60% sulphuric acid is often a good method to effect desulphonation,[39] but this proved to be useless when applied to the above product.

In the Bally synthesis, the effective condensing species is anthrone, formed by the copper/sulphuric acid reduction (in situ) of anthraquinone. It is feasible that sulphonation may have occurred during this part of the synthesis, and an alternative means of reduction was therefore sought.

The reduction of anthraquinones to anthrones was first successfully studied by Barnett and Matthews,[40] who employed sulphuric acid and aluminium powder to

reduce 1-chloroanthraquinone to 1-chloro-9-anthrone (XXXV). Methods of reduction avoiding the use of sulphuric acid are, however, available. Thus, the above quinone is reduced to the isomeric anthrone (XXXVI) by means of tin and fuming hydrochloric acid.(41)




Hydroxy anthraquinones are reduced by stannous chloride/hydrochloric acid;(42) a similar reduction of the parent quinone may be effected by heating with glucose and alkali,(43) whilst the enolic form, anthranol, has been prepared by catalytic hydrogenation of anthraquinone, at high temperatures.(44)

Of these reductions, all of which are reported as proceeding in good yield, tin and hydrochloric acid was employed to effect the reduction of 1-phenylanthraquinone. It was hoped that the bulky phenyl group would shelter the adjacent carbonyl group, and that the product would be 1-phenyl-9-anthrone.

The material so obtained gave a strong Liebermann

Anthrone test, but the analysis figures lay between those of the anthrone and starting material. This indicated the presence of some unreduced anthraquinone, despite a prolonged period of reduction.

Fractional crystallisation did not effect further purification, whilst chromatographic methods resulted in chemical change due to the tendency of anthrones to undergo aerial oxidation in an alkaline medium.(41) The melting point in conjunction with a mixed melting point served to distinguish the compound from starting material.

Anthrones are capable of existing in tautomeric equilibrium with the enolic form, which can be acetylated. The suspected phenyl-anthrone could not be acetylated or benzoylated. This lack of reactivity may be ascribed to two sources, and it is probable that either or both of these constitute an adequate explanation.

(a) The direction of the equilibrium might be such that the keto form greatly predominates, to the exclusion of anthranol formation. (The equilibrium mixture of anthrone contains only 11% of the enol at room temperatures.)

(b) Should such anthranol formation occur, the steric effect of the phenyl substituent would hinder chemical attack at the -OH group.

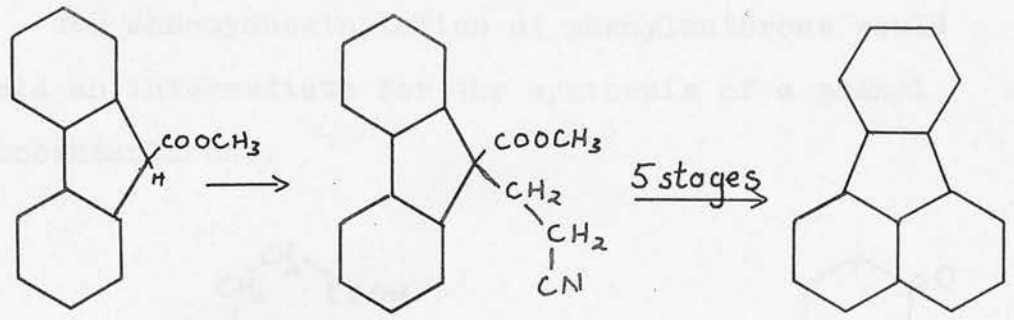
The second explanation implies that the desired

carbonyl group had been reduced.

The impure 1-phenyl-9-anthrone was treated with glycerol and sulphuric acid, the reaction time being reduced from 10½ hours to 2 hours. The formation of a black granular mass, exhibiting identical properties to the material previously obtained, indicated that the sulphonation problem was not likely to be overcome, and this route to 8-phenyl-mesobenzanthrone was therefore abandoned. In retrospect, the replacement of sulphuric acid by a milder cyclising agent, for example, polyphosphoric acid, might be worth future investigation.

A well known feature of fluorene chemistry is the ability of this compound and its substituted derivatives to undergo Michael addition at the methylene group with acrylonitrile.

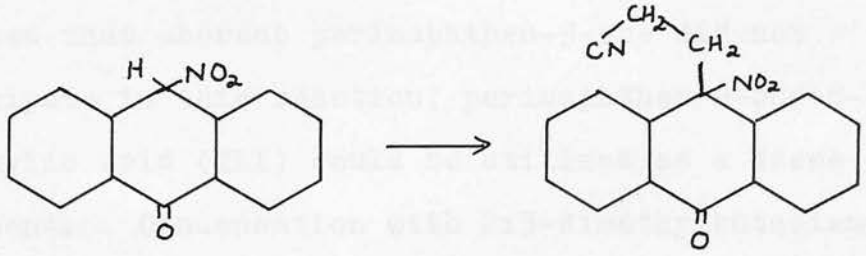
In the case of fluorene itself, the reaction is so facile, that two molecules of acrylonitrile add on with alacrity, and suitable blocking groups, e.g. carbomethoxy, must be present to secure mono-addition (XXXVII).[45] Such products are intermediates in a synthesis of fluoranthene (XXXVIII).




XXXVII XXXVIII

Similarly, acrylonitrile condenses with anthrone, in the presence of a strongly alkaline catalyst (e.g. Triton B), to give on alkaline hydrolysis, the bis-carboxyethyl anthrone.(46)

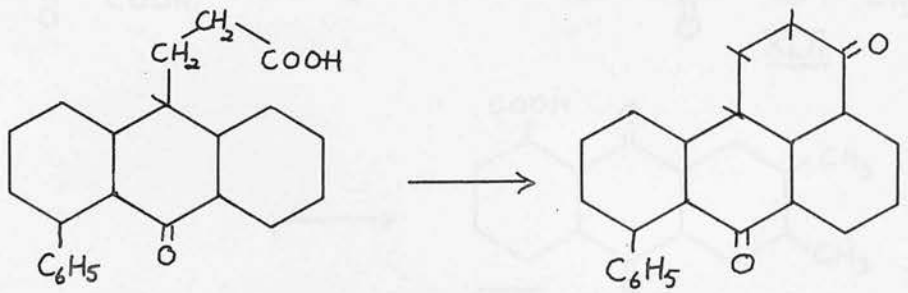
Prolonged heating of 9-nitroanthrone (XXXIX) with acrylonitrile is reported(47) to yield 9-nitro-9-$\beta$-cyanoethylanthrone (XL) but this is the only recorded case of anthrone monocyanoethylation.




XXXIX XL

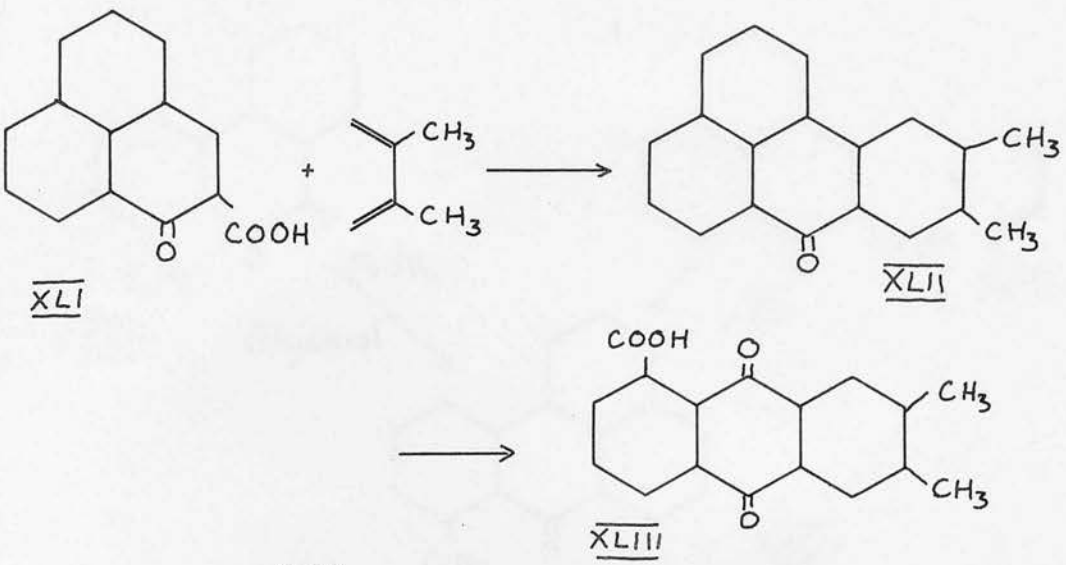
A generalisation by Campbell(48) shows that higher reaction temperatures favour monocyanoethylation, a quoted example being the case of benzyl cyanide.

The monocyanoethylation of phenylanthrone would yield an intermediate for the synthesis of a phenyl mesobenzanthrone.




Unfortunately no condensation occurred between acrylonitrile and the anthrone, even at elevated temperatures in the presence of Triton B or sodium ethoxide, and starting material was invariably recovered.

The Diels-Alder reaction has proved an exceptionally useful means of synthesising aromatic and hydro-aromatic ring systems. Fieser and Newton[49] observed that whereas perinaphthen-9-one did not participate in this reaction, perinaphthen-9-one-8-carboxylic acid (XLI) could be utilised as a diene component. Condensation with 2:3-dimethylbutadiene yielded 9:10-dimethylmesobenzanthrone (XLII), orientated by oxidation to the acid (XLIII).

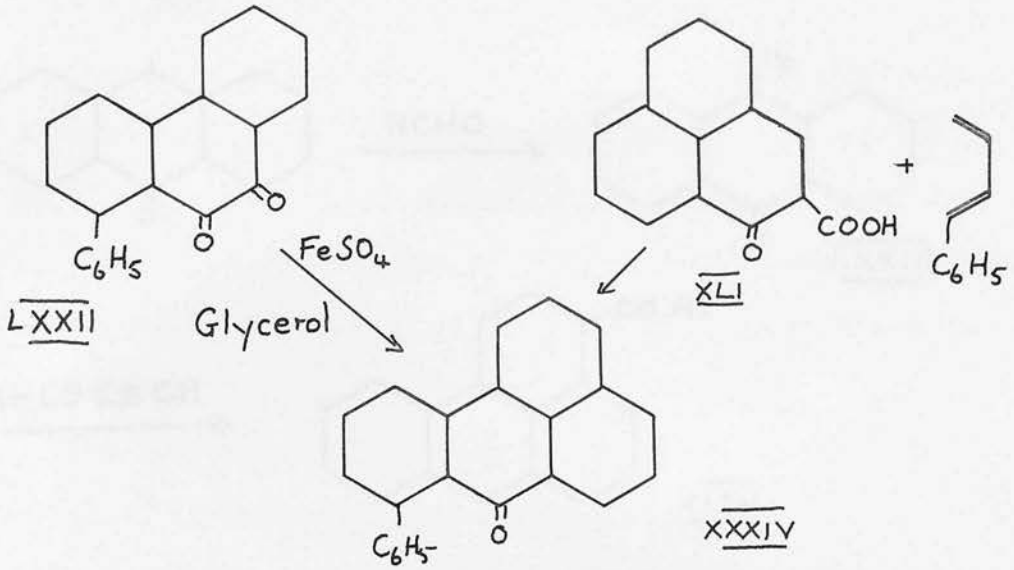



XLI XLII XLIII

R.A. Wall[37] applied this method to the synthesis of XXXIV, and condensed (XLI) with 1-phenyl-butadiene. Somewhat surprisingly, only one compound was formed, oxidation of which did not yield any identifiable products. Steric considerations led to the belief that this compound was 8-phenylmesobenzanthrone, and not the 11-isomer.

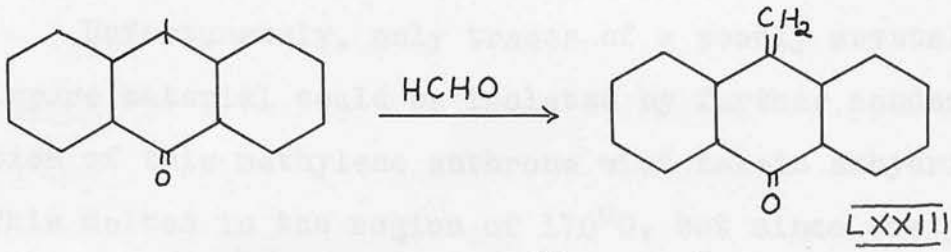
By condensation of phenanthraquinone with glycerol, in the presence of anhydrous ferrous sulphate and 70% sulphuric acid, Turski[50] prepared the unsubstituted ketone.

Carrying out a similar reaction with 1-phenyl-phenanthraquinone (LXXII), Wall achieved the unequivocal synthesis of 8-phenylmesobenzanthrone, and demonstrated that the compound obtained from this reaction was identical with that derived from the Diels-Alder condensation.

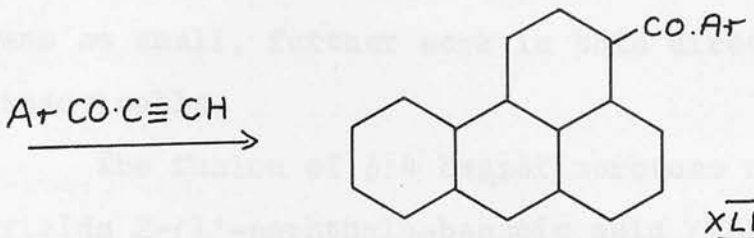



These syntheses are only of passing interest, since the yield of (XXXIV) is, in both cases, extremely poor. Other methods must therefore be explored in order to secure a reasonable quantity of such compounds.

A further feature of the chemistry of anthrones is the base catalysed condensation of such substances with carbonyl groups. Thus anthrone itself interacts readily with formaldehyde in the presence of pyridine, to form methyleneanthrone (LXXIII).[51,52] Condensation products of this type undergo Diels-Alder reactions by virtue of their potential 1:3 diene system. Interaction of (LXXIII) with acyl acetylenes yields[53] 3-acylmesobenzanthrones (XLIV), and similar condensations with indene and ethyl cinnamate have been reported.[54]

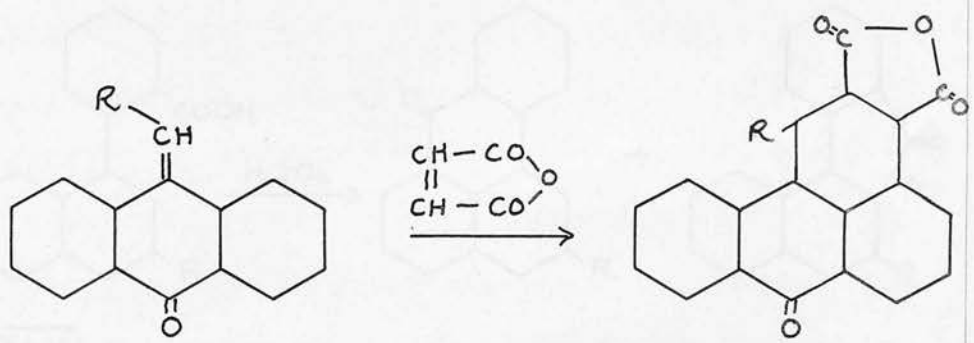



LXXIII




XLIV

By controlled condensation of maleic anhydride with substituted methyleneanthrones of type XLV, Clar[52] has obtained products (XLVI) which might prove intermediates in the synthesis of substituted mesobenzanthrones.




XLV XLVI

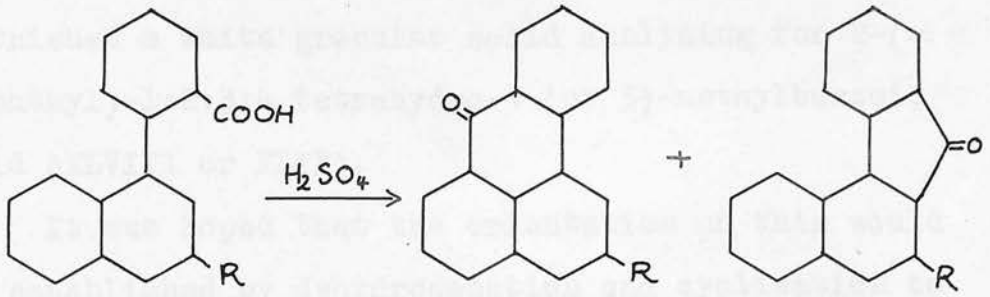
Little work appears to have been performed in preparing methyleneanthrones substituted in the aromatic nucleus, and no reference is made to the condensation of such compounds with maleic anhydride.

A pure substance, analysing for phenyl-methyleneanthrone, was obtained by condensing 1-phenyl-9-

anthrone with formaldehyde.

Unfortunately, only traces of a poorly crystalline impure material could be isolated by further condensation of this methylene anthrone with maleic anhydride. This melted in the region of 170°C, but since the yield was so small, further work in this direction was deemed inadvisable.

The fusion of 3:4 benzofluorenone with alkali yields 2-(1'-naphthyl)-benzoic acid (XLVII, R = H).(55) In this latter compound, rotation about the bond joining the 'phenyl' and 'naphthyl' halves of the molecule may occur, and recyclisation (with sulphuric acid) provides a separable mixture of the starting benzofluorenone and mesobenzanthrone.




XLVII

Similarly the recyclisation of 1-phenyl-2':3-naphthalene dicarboxylic acid (XLVII, R = COOH) results in the formation of mesobenzanthrone-2-carboxylic acid, from which the otherwise difficultly accessible 2-acyl and 2-aryl derivatives may be prepared.

The cyclisation of $\beta$-(1-naphthyl)-propionic acids

has been studied by Ansell,[56] who showed that the use of anhydrous hydrogen fluoride gave a mixture of perinaphthanones and 3:4 benzohydrindones, separable by chromatography, and identifiable by oxidation.

It is apparent that the synthesis of substituted mesobenzanthrones might be accomplished by cyclising the appropriately substituted naphthyl-benzoic acid. Should the benzofluorenone be formed in any quantity, this might be converted to a mesobenzanthrone by Schaarschmidt's method.

The synthesis of the desired intermediates was again attempted by means of a Diels-Alder reaction.

Prolonged heating of 2-(α-naphthyl)-acrylic acid with isoprene in a sealed Cairns tube at 180°C furnished a white granular solid analysing for 2-(α-naphthyl)-1:2:3:4 tetrahydro-4-(or 5)-methylbenzoic acid (XLVIII or XLIX).

It was hoped that the orientation of this would be established by dehydrogenation and cyclisation to either of the known 9- or 10-methyl-mesobenzanthrone (L or LI).

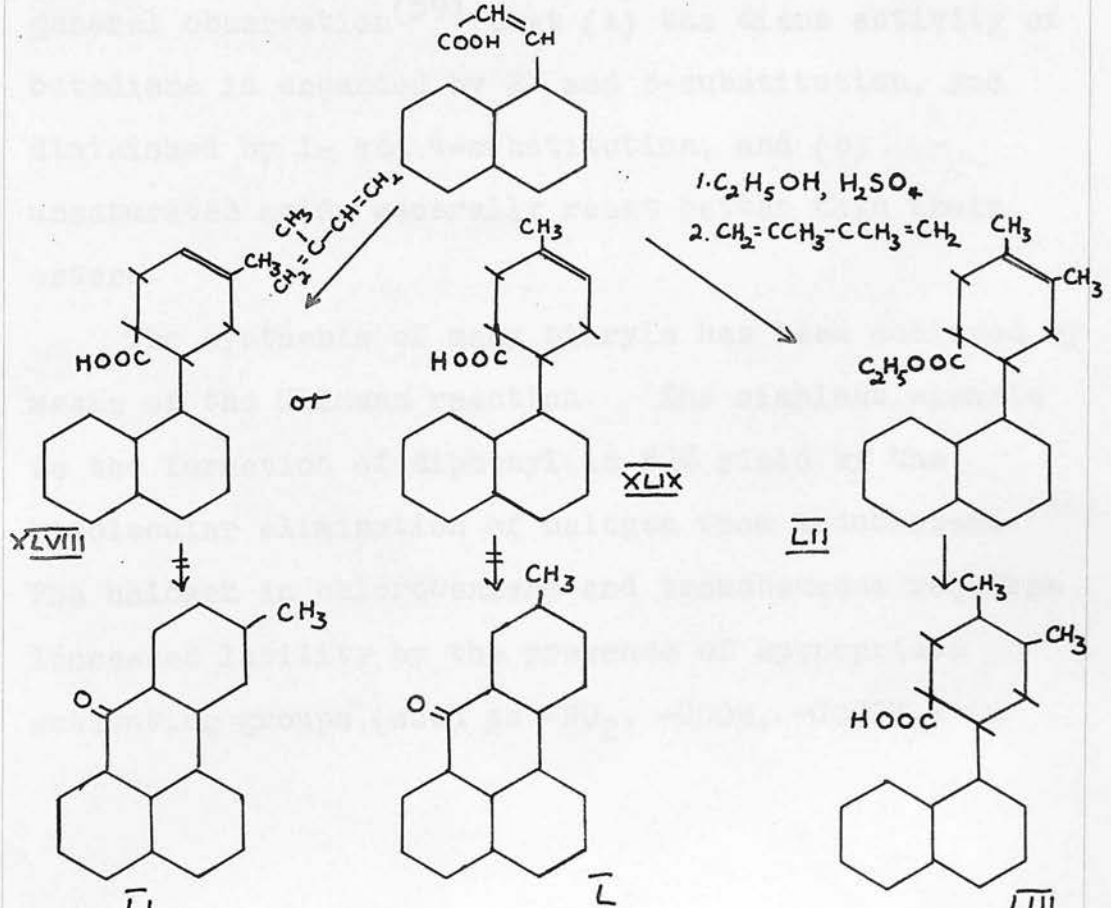
Dehydrogenation was not achieved either by heating with chloranil in xylene, or by boiling with nitrobenzene. Starting material was recovered from the second, but not from the first method.

Unsuccessful attempts to effect cyclisation were then made, using sulphuric acid. The failure to

isolate any solid product can hardly be ascribed to sulphonation, since the reaction time (1 hour) and temperature (50°C) were so controlled as to make such attack improbable.

A similar condensation of 2:3 dimethylbutadiene with the ethyl ester of 2-(α-naphthyl)-acrylic acid gave the hydroaromatic ester (LII) in good yield. The acid (LIII) obtained by hydrolysis of this again proved resistant to dehydrogenation, and only tars of the type described by Allen et al[57] were encountered.

The cyclisation of 2-(α-naphthyl)-benzoic acid by concentrated sulphuric acid and by aluminium chloride on the acid chloride has been carried out,[58] but no pure cyclised product could be obtained by treatment of (LIII) with these reagents, or with polyphosphoric acid.



It must be mentioned that the aluminium chloride cyclisation provided traces of an amorphous brown solid whose red solution (green fluorescence) in sulphuric acid indicated that some cyclisation to the meso-benzanthrone had taken place.

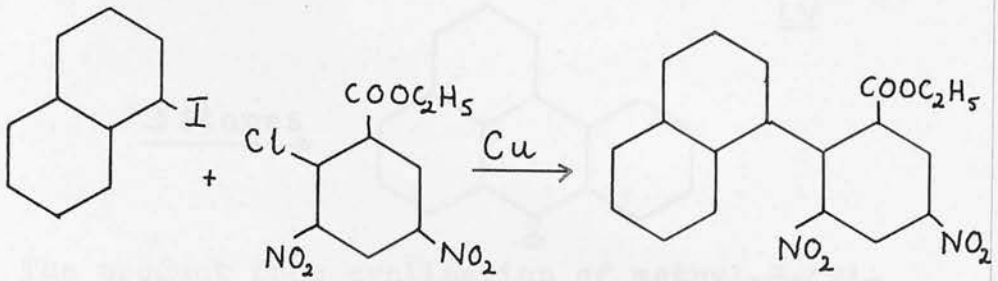
In spite of these adverse results, attempts were made to condense 2-(α-naphthyl)-acrylic acid with phenylbutadiene. This reagent is readily polymerised, hence milder condensation conditions, and a slight excess of the diene, were employed. No interaction occurred under such circumstances, and even the most drastic conditions, whereby the acid was heated for 67 hours at 175°C in a sealed tube, with 200% excess of the diene, failed to give condensation.

These results, although negative, agree with the general observation[59] that (a) the diene activity of butadiene is enhanced by 2- and 3-substitution, and diminished by 1- and 4-substitution, and (b) β-unsaturated acids generally react better than their esters.

The synthesis of many biaryls has been achieved by means of the Ullmann reaction. The simplest example is the formation of diphenyl in 82% yield by the bimolecular elimination of halogen from iodobenzene.[60] The halogen in chlorobenzene and bromobenzene requires increased lability by the presence of appropriate activating groups (such as $-NO_2$, $-COOH$, $-COOCH_3$) in

order that such compounds may be effectively condensed.

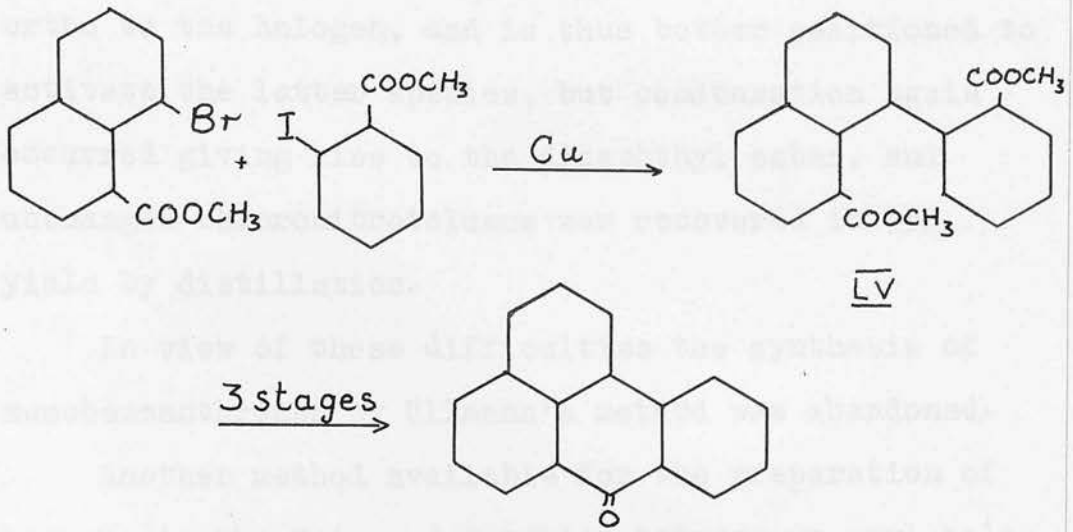
The synthesis also lends itself to the preparation of unsymmetrical biaryls. Thus ethyl 2,4-dinitro-6-chlorobenzoate condenses with 1-iodonaphthalene[61] to give a 53% yield of the unsymmetrical compound (LIV).




LIV

However this reaction is exceptional in that it provides only one product, and in most other reactions a mixture of symmetrical and unsymmetrical products is generally encountered.

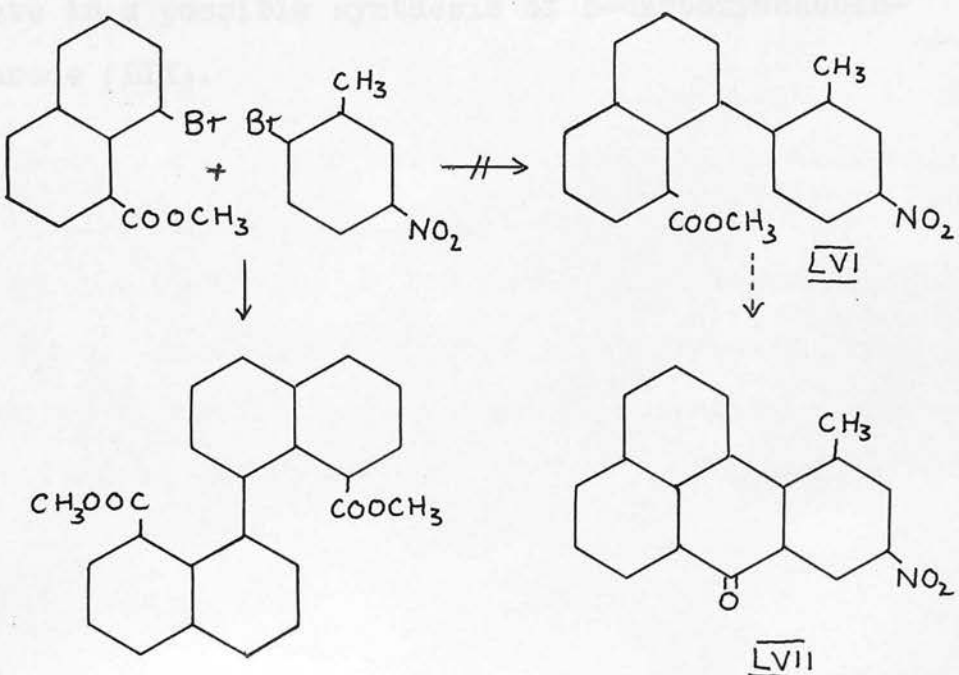
Rule and co-workers[62] have utilised the reactivity of the bromine atom in methyl-8-bromo-1-naphthoate in a synthesis of mesobenzanthrone. Condensation of the former with methyl-2-iodo-benzoate gave the unsymmetrical product (LV) which hydrolysed, cyclised, and decarboxylated to the desired ketone.




LV

The product from cyclisation of methyl-8-(2'-methyl-4'-nitro-)-phenyl-1-naphthoate (LVI) would thus be 9-nitro-11-methylmesobenzanthrone (LVII).

Attempts to isolate (LVI) by interaction of methyl-8-bromo-1-naphthoate with 2-bromo-5-nitrotoluene were baulked by preferential formation of the symmetrical dimethyl-1-1'-dinaphthyl-8-8'-dicarboxylate (LVIII), separated from unreacted nitrobromotoluene (recovered in 98% yield) by chromatography.




LVIII LVI LVII

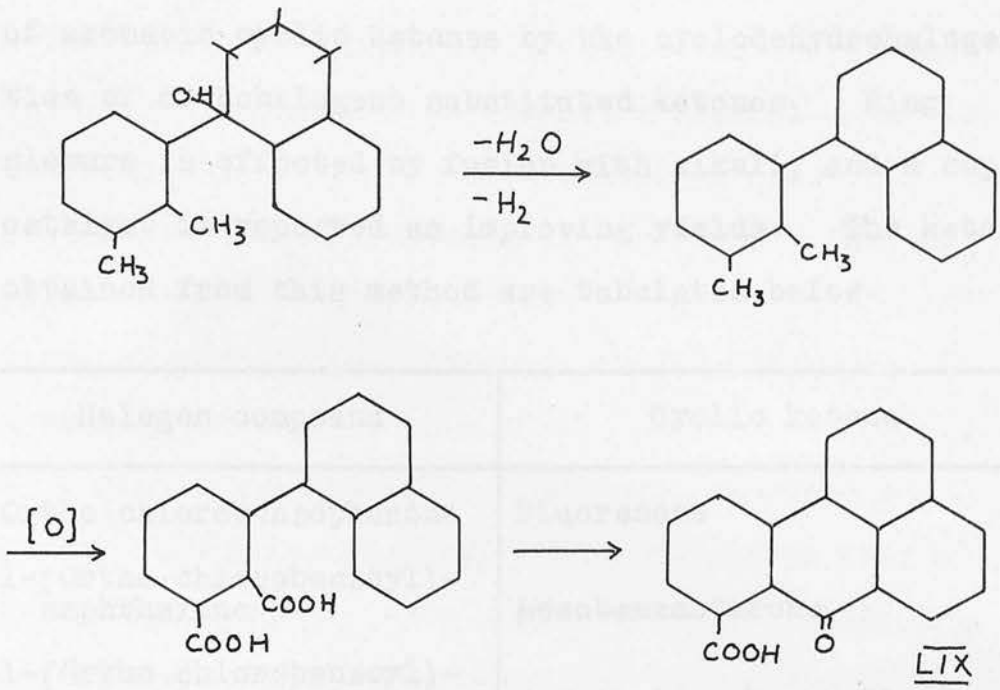
For 4-chloro-3-nitrotoluene, the nitro group is ortho to the halogen, and is thus better positioned to activate the latter species, but condensation again occurred giving rise to the dinaphthyl ester, and unchanged chloronitrotoluene was recovered in 95% yield by distillation.

In view of these difficulties the synthesis of mesobenzanthrones by Ullmann's method was abandoned.

Another method available for the preparation of biaryls is the Grignard reaction between an aryl halomagnesium compound and a cyclic ketone. The product of this reaction when dehydrated and dehydrogenated would yield the required biaryl.

The apparent advantage of this method over the Ullman synthesis is the smaller probability of encountering a mixture of products.

Thus tetralone might be expected to interact with 2,3 dimethylphenylmagnesiumiodide to give an intermediate in a possible synthesis of 8-carboxymesobenzanthrone (LIX).




LIX

In attempting this reaction sequence, Wall(37) found that no unsymmetrical product could be isolated from the Grignard stage, and obtained a substance with properties similar to the "abnormal" product, 1-oxo-2-(1'-tetralylidene)-1:2:3:4 tetrahydronaphthalene, previously isolated from certain tetralone Grignard reactions.(63)

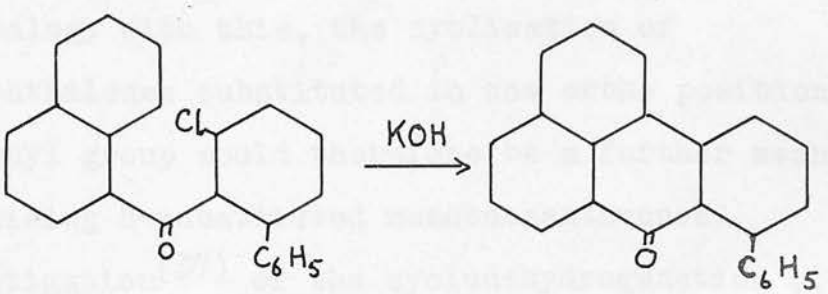
The results from the Grignard reagent derived from 3-bromo-2-chlorotoluene and from 2-bromochlorobenzene were equally unpromising, and in the light of these results, the synthesis of 3-bromo-2-chlorobiphenyl, and reaction of the Grignard reagent with tetralone was considered an unprofitable method of preparing 8-phenylmesobenzanthrone.

I.G. Farben Industrie[64] have patented a synthesis of aromatic cyclic ketones by the cyclodehydrohalogenation of orthohalogeno substituted ketones. Ring closure is effected by fusion with alkali, and a copper catalyst is reported as improving yields. The ketones obtained from this method are tabulated below.

| Halogen compound | Cyclic ketone |
|---|---|
| Ortho-chlorobenzophenone | Fluorenone |
| 1-(Ortho-chlorobenzoyl)-naphthalene | Mesobenzanthrone |
| 1-(Ortho-chlorobenzoyl)-2-methylnaphthalene | 6-Methylmesobenzanthrone |
| 1-(Ortho-chlorobenzoyl)-2:6-dimethylnaphthalene | 2:6-Dimethylmesobenzanthrone |

From these results it is seen that where formation of a 5- or 6-membered ring is possible, cyclisation so occurs that the mesobenzanthrone is formed in preference to the fluorenone.

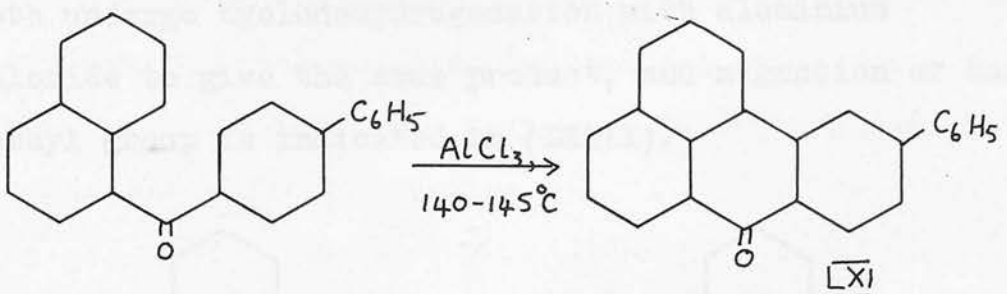
By such a method, 8-phenylmesobenzanthrone might be prepared from 2-(1'-naphthyl)-3-chlorodiphenyl (LX).




LX

The preparation of LX was thought likely to present some difficulties, and since this idea was conceived late on in the research, insufficient time was available to study the synthesis of this compound, or to establish the optimum cyclisation conditions, which are not mentioned in the patent. Future work directed along these lines may result in a profitable synthesis of 8-, 9-, 10-, or 11-substituted ketones.

Scholl and Seer[65a] cyclodehydrogenated 1-benzoylnaphthalene by fusion with aluminium chloride. In this case cyclisation again occurs yielding mesobenzanthrone, rather than 1:2-benzofluorenone, as the main product. The same authors[65b] extended this method and report the cyclisation of 1-(4'-phenyl)-benzoylnaphthalene to 10-phenylmesobenzanthrone (LXI).




LXI

By analogy with this, the cyclisation of benzoylnaphthalenes substituted in the ortho position of the phenyl group would therefore be a further means of synthesising 8-substituted mesobenzanthrones.

Investigation[37] of the cyclodehydrogenation of

1-(2'-phenyl-benzoyl)-naphthalene (LXII) indicated that the compound isolated (in poor yield) was, in fact, mesobenzanthrone. Evidence supporting this conclusion came from

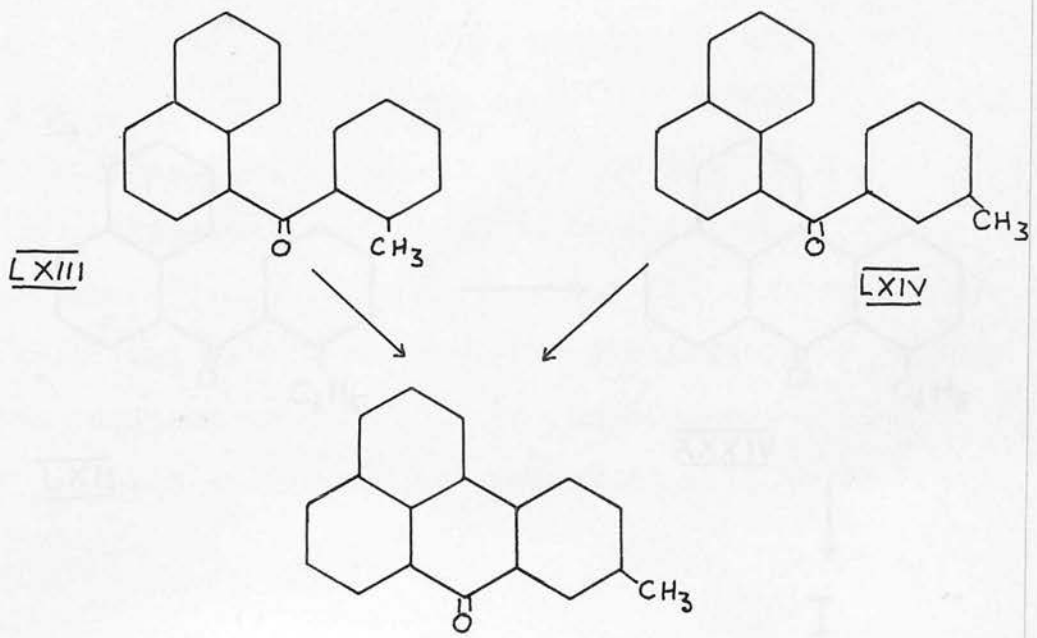
(a) Meltingpoint (a mixed melting point with mesobenzanthrone being undepressed);

(b) The ultraviolet absorption spectrum;

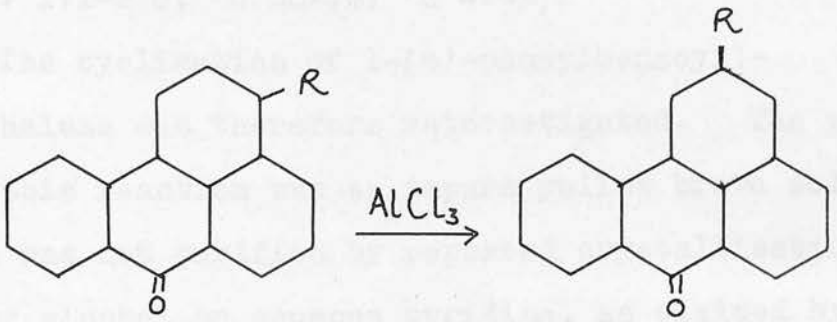
and (c) Analytical data.

Each of these physical properties bore a close resemblance to those possessed by the unsubstituted ketone.

Group migration in the presence of aluminium chloride is not uncommon. The work of Scholl, and of Schmidlin[66] has shown that 1-(2'-methyl-benzoyl)-(LXIII), and 1-(3'-methyl-benzoyl)-naphthalene (LXIV) both undergo cyclodehydrogenation with aluminium chloride to give the same product, and migration of the methyl group is indicated in (LXIII).

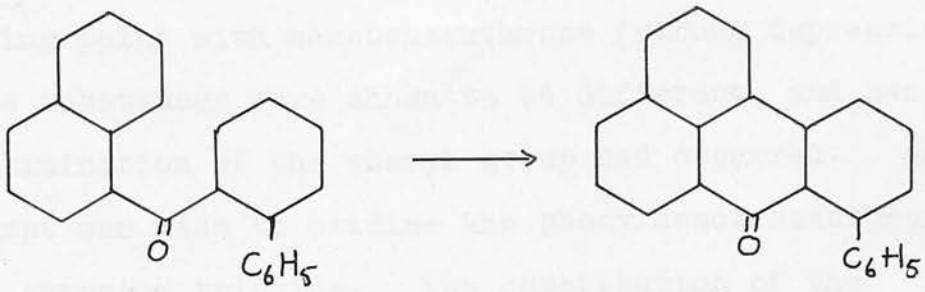


The cyclisation of the 4- and 2-methyl-1-benzoyl-naphthalenes, was reported[67] as yielding two distinct products, yet subsequent work[68] has shown that only one compound is formed, corresponding to migration of the 2-methyl group. Further, aluminium chloride is effective in converting 3-substituted mesobenzanthrones (LXV, R = $-C_6H_5$, $-CH_3$) into the corresponding 2-isomer (LXVI).[38,69]




LXV LXVI

Group migrations must consist essentially of a two stage elimination-recombination process, and it would seem that for (LXII), the second stage of this does not take place.




LXII XXXIV

I

From a consideration of these results it is possible that migration or elimination of the phenyl group had occurred during the ring closure of 1-(4'-phenylbenzoyl)-naphthalene.

Scholl and Seer give no yield of product, and omit the very necessary orientation by oxidation. Further the melting point (170-1°C) and analysis (C 89.9%; H 5.2%) do not differ greatly from mesobenzanthrone (M.Pt. 171-2°C; C 88.7%; H 4.4%).

The cyclisation of 1-(4'-phenylbenzoyl)-naphthalene was therefore reinvestigated. The product from this reaction was an impure yellow brown solid, which was not purified by repeated crystallisation from either alcohol or aqueous pyridine, as claimed by Scholl.

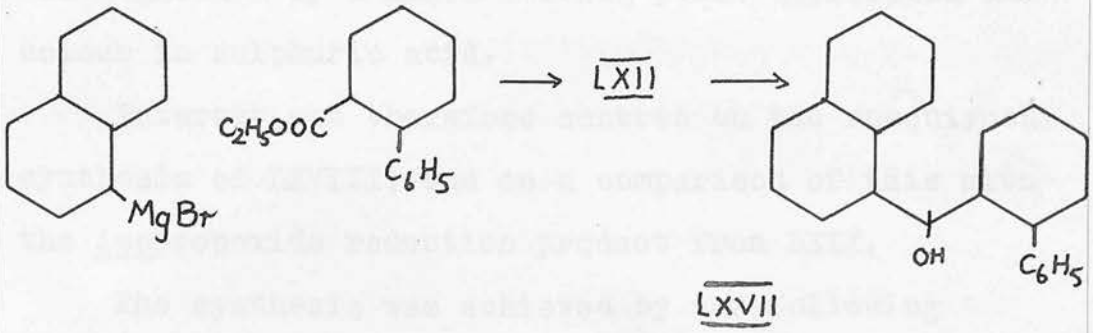
Repeated chromatography in benzene gave orange yellow needles, melting over a two degree range. A solution of the substance, which was not pure enough to permit analysis or spectral examination, in sulphuric acid gave the characteristic mesobenzanthrone red colour, with green fluorescence. By means of a mixed melting point with mesobenzanthrone (strong depression) these substances were shown to be different, and hence no elimination of the phenyl group had occurred. An attempt was made to oxidise the phenylmesobenzanthrone with chromium trioxide. The constitution of the substituted anthraquinone carboxylic acid would

indicate whether or not group migration had occurred.

Unfortunately the limited amount of starting material available did not permit the isolation of any solid material.

In his examination of the ring closure of (LXII), Wall approached the synthesis of this compound by two routes:

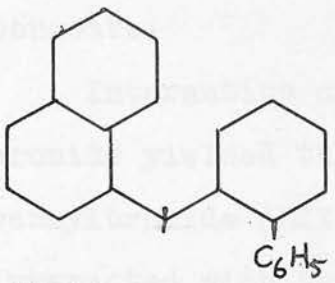
1. The Grignard solution from 2-iododiphenyl was allowed to interact with 1-naphthonitrile. In this case the ketone was obtained; due to the strong blanketing effect of the two aromatic nuclei, a considerable diminution in ketonic activity was observed. The compound did not form an oxime, and only forcing conditions permitted the isolation of an impure dinitrophenylhydrazone.
2. 2-Carbomethoxydiphenyl when treated with $\alpha$-naphthylmagnesiumbromide gave a substance melting considerably higher (154-5°C) than the material obtained by the first route (129-30°C). The analysis and ultraviolet absorption spectra indicated that the excess Grignard reagent had effected reduction of the ketone to the carbinol (LXVII), a reaction noted in the case of the unsubstituted benzoylnaphthalene and related compounds.(70)




LXVII

For correlation purposes, Wall had recourse to the preparation of (LXVII) by reduction of (LXII), and found that certain reagents expected to promote the reaction carbonyl →carbinol (i.e. lithium aluminium hydride and potassium borohydride) were ineffective.

On attempting the reduction by the Meerwein-Ponndorf method, employing aluminium isopropoxide, the expected carbinol was not formed, but a compound (M.Pt. 88.5-96.5°C) resisting complete purification, yet analysing for the hydrocarbon (LXVIII).




LXVIII

Such abnormal reductions have only been observed three times previously: with 9:9-dimethylanthrone-10, with anthrone, and with mesobenzanthrone.

Examination, in the present research, of the similar reduction of 1-(4'-phenylbenzoyl)-naphthalene showed that the 'normal' product (i.e. the carbinol) was produced. Somewhat surprisingly, this melted some

twenty degrees below the ketone, from which it was distinguished by a mixed melting point depression and colour in sulphuric acid.

Interest was therefore centred on the unequivocal synthesis of LXVIII, and on a comparison of this with the isopropoxide reduction product from LXII.

The synthesis was achieved by the following reaction sequence.

Ortho phenylbenzylalcohol (LXIX) was prepared by lithium aluminium hydride reductions of orthophenylbenzoic acid and its ethyl ester; previous reports[71,72] mention this as being a high boiling oil, but, in the present case, a low melting white solid was obtained, analysing for the alcohol, and yielding a 3:5-dinitrobenzoate.

Interaction of (LXIX) with ethereal hydrogen bromide yielded the strongly lachrymatory orthophenylbenzylbromide (LXX), the Grignard reagent of which interacted with tetralone to give 1-(2'-phenylbenzyl)-3:4-dihydronaphthalene (LXXI), as indicated by analysis, and by decolouration of permanganate and bromine in carbon tetrachloride.

The spontaneous dehydration of carbinols derived from Grignard reactions is not uncommon, although such dehydration is normally reported as occurring

(a) When the reaction is carried out at elevated temperatures;

or (b) When an acidic hydrolysis of the Grignard complex is employed.(73)

The spontaneous dehydration of the intermediate from α-tetralone and phenylmagnesiumbromide(74) in the presence of hydrochloric acid has been similarly noted as yielding 1-phenyl-3:4-dihydronaphthalene.

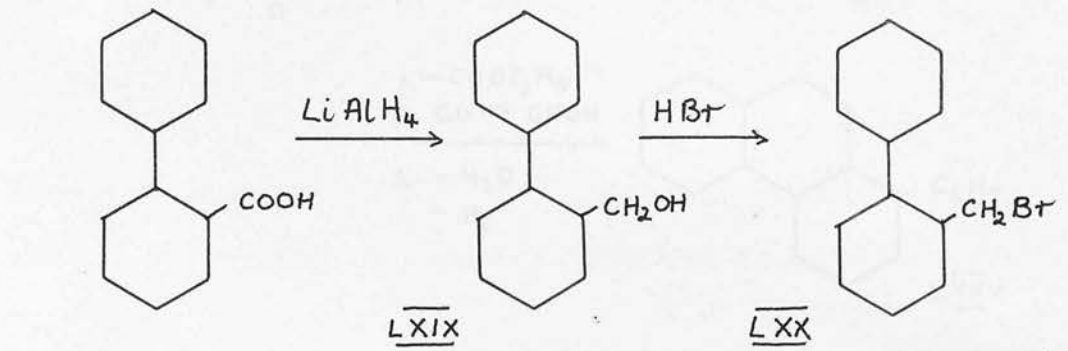
In the present case dehydration has most likely occurred to give endocyclic unsaturation, as opposed to the exocyclic ethylenic compound.

Dehydrogenation of (LXXI) to (LXVIII) was readily effected in 80% yield, in the presence of 30% palladium-charcoal catalyst. The same hydrocarbon was also prepared in poor yield by a Friedel-Crafts reaction of (LXX) with naphthalene, using as catalyst, anhydrous stannic chloride.

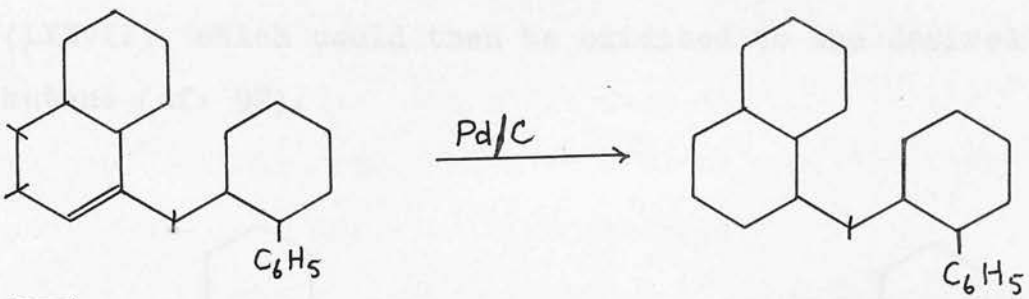
Since (LXVIII) melted sharply at 120°C, was easily isolated, and appeared to be completely pure, little reliance can be placed on the homogeneity of Wall's compound.

Attempts to isolate o-phenylbenzoylchloride by interaction of the acid with thionyl chloride were unsuccessful. A good yield of fluorenone invariably resulted, due to cyclisation of the (presumably formed) acid chloride on distillation. No mention has been made of this facile cyclisation by previous workers. Under Friedel-Crafts conditions at room temperatures in the presence of a large excess of naphthalene, this

cyclisation occurred in preference to an intended acylation, and a separation of the unchanged naphthalene from fluorenone was achieved chromatographically.

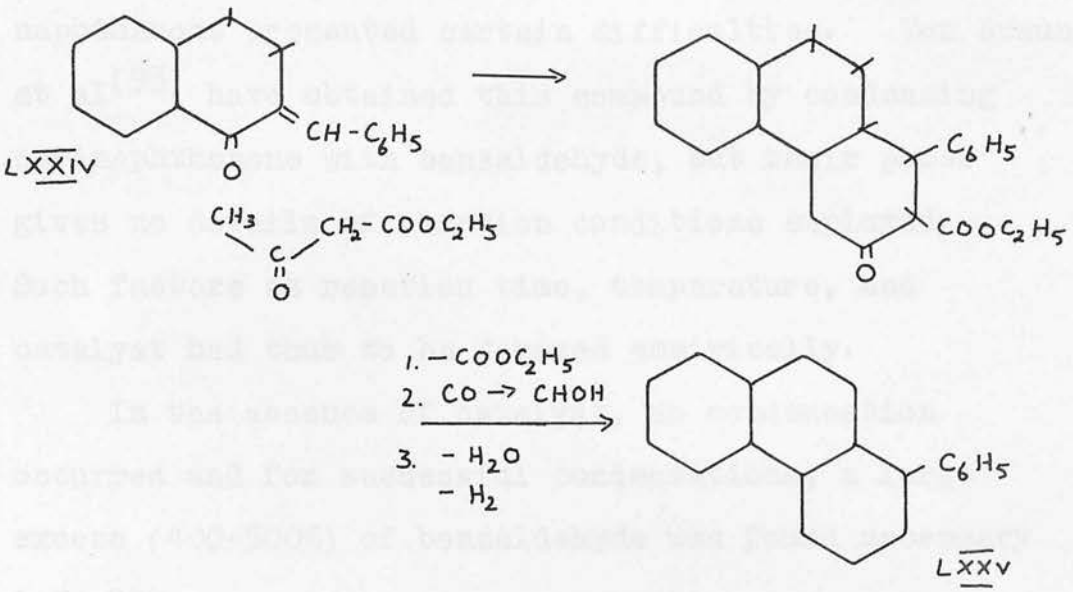



LXIX LXX

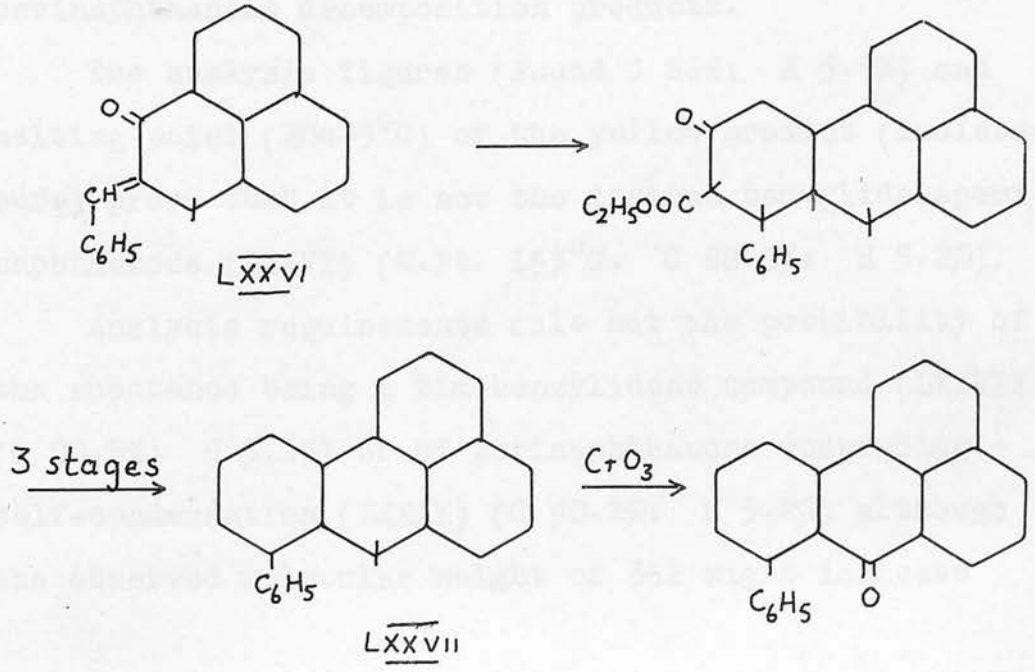



LXXI LXVIII

An excellent synthesis of alicyclic ring systems is that discovered by A. Michael (90). In the base catalysed reaction bearing his name, $\alpha$-$\beta$ -unsaturated carbonyl compounds are condensed with substances containing the so-called 'activated' methylene group. A specific case is the 4-stage synthesis of 1-phenylphenanthrene (LXXV) from 2-benzylidenetetralone (LXXIV) (91).




The addition of ethylacetoacetate to benzylidene-perinaphthanone (LXXVI) might, by analogy, provide a convenient synthesis of 8-phenylmesobenzanthrene (LXXVII), which could then be oxidised to the desired ketone (cf. 92).



Unfortunately the preparation of benzylideneperinaphthanone presented certain difficulties. Von Braun et al[93] have obtained this compound by condensing perinaphthanone with benzaldehyde, but their paper gives no details of reaction conditions employed. Such factors as reaction time, temperature, and catalyst had thus to be derived empirically.

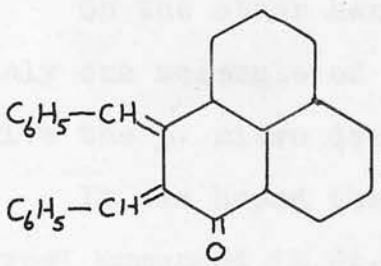
In the absence of catalyst, no condensation occurred and for successful condensations, a large excess (400-500%) of benzaldehyde was found necessary (cf. 94).

Of all the reaction media employed (4% alcoholic KOH, pyridine/piperidine, 80% sulphuric acid, acetic anhydride) only the first named was successful, inasmuch that it permitted isolation of a yellow crystalline solid. The black tars and oils which accompanied this were shown by a blank experiment to be perinaphthanone decomposition products.

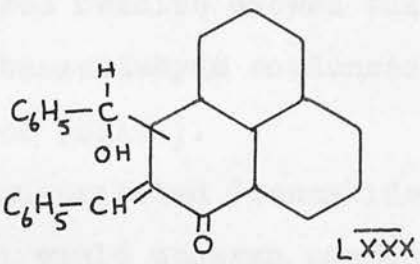
The analysis figures (Found C 86%; H 5.5%) and melting point (204-5°C) of the yellow product (isolated pure) prove that it is not the desired benzylideneperinaphthanone (LXXVI) (M.Pt. 163°C. C 88.9%; H 5.2%).

Analysis requirements rule out the possibility of the substance being a bis-benzylidene compound (LXXVIII) (C 90.5%; H 5.1%) or of perinaphthanone undergoing self-condensation (LXXIX) (C 90.1%; H 5.2%) although the observed molecular weight of 362 might indicate

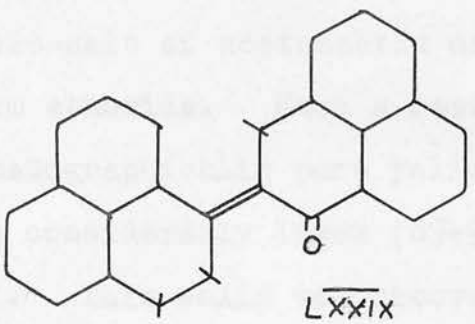
either (LXXVIII) (M.Wt. 358) or (LXXIX) (M.Wt. 346). Overall a much better agreement exists with a compound of structure (LXXX) (M.Wt. 376, C 86.2%; H 5.4%), although such products have not been previously encountered.




LXXVIII




LXXX




LXXIX

The compound did not form a dinitrophenylhydrazone but the oxime (obtained under forcing conditions) gave analysis figures which supported structure (LXXX).

| | | | |
|---|---|---|---|
| Found | C 82.5% | H 5.4% | N 3.1% |
| $C_{27}H_{21}NO_2$ | C 82.8% | H 5.4% | N 3.6% |

p. Chlorobenzaldehyde similarly condensed with perinaphthanone. Again, a large excess of the aldehyde was required to ensure a good yield, although when the excess was limited to but 20%, a small quantity of condensation product was isolated. Once more, analytical data corresponded best to the

requirements of the chlorinated analogue of (LXXX).

| | | | |
|---|---|---|---|
| Found | C 71.6% | H 4.9% | Cl 15.8% |
| $C_{20}H_{13}OCl$ | 78.9% | 4.3% | 11.6% |
| $C_{27}H_{16}OCl_2$ | 75.9% | 3.8% | 16.6% |
| $C_{27}H_{18}O_2Cl_2$ | 72.7% | 4.1% | 15.9% |

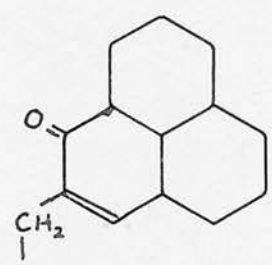
On the other hand, analyses results showed that only one molecule of p. nitrobenzaldehyde condensed, to give the p. nitro derivative of (LXXVI).

It was hoped that the unsubstituted "benzylidene-type" compound (M.Pt. 204-5°C) would undergo condensation with the sodio-salt of acetoacetic ester, in the presence of sodium ethoxide. Such a reaction furnished a chromatographically pure yellow crystalline substance melting considerably lower (89-90°C) than starting material. This solid was recovered unchanged from conditions expected to effect a decarbethoxylation. Two inferences are possible from this result. Either (1) an elimination of $-COOC_2H_5$ had occurred during the Michael addition, or (2) no addition of acetoacetic ester had taken place at all, but that the benzylidene-perinaphthanone had decomposed to some simpler compound in the presence of sodium ethoxide. The first explanation is but remotely probable, since no similar case has been recorded. The closest analogy available is the loss of $-COOC_2H_5$ encountered on distilling 1a:1:2:3:9:10-hexahydro-2-carbethoxy-3-ketophenanthrene.(91)

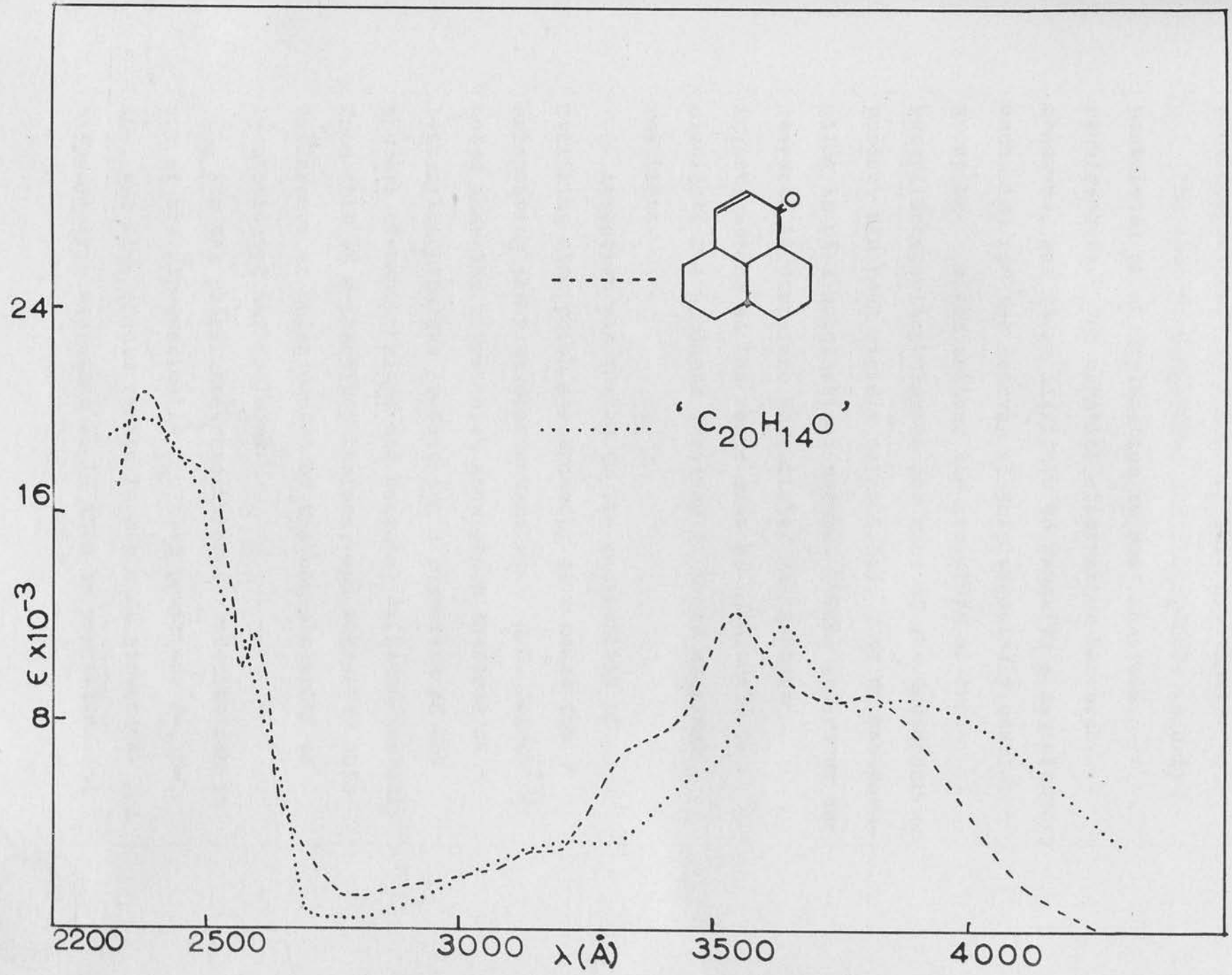
Analysis figures indicated that the compound

(M.Pt. 89-90°C) possessed a formula of $C_{20}H_{14}O$; this was confirmed by a Molecular Weight determination (Rast Method. Found 239-262, Required 270). Moreover the fact that it was obtained by refluxing the "benzylideneperinaphthanone" with sodium ethoxide ("blank" test) demonstrated conclusively that a molecular cleavage, probably involving loss of $C_6H_5CHOH$-, had taken place in preference to condensation with acetoacetic ester. Similarly, the bis-p. chlorobenzylideneperinaphthanone, when heated with sodium and ethanol in the presence or absence of acetoacetic ester, gave in each experiment the same product M.Pt. 120-1°C, analysing for $C_{20}H_{13}OCl$. It is not possible to assign a structure to the product M.Pt. 89-90°C (or to the chloro-analogue) with any certainty, yet the limited evidence available does not preclude its being a geometrical isomer of the quoted literature compound (M.Pt. 163°C) (LXXVI). In the closely analagous chalkone series, such stereoisomers have been isolated and shown to be interconvertible.(95)

An alternative possibility is that (LXXX) has been converted to the tautomeric form of (LXXVI), benzylperinaphthenone (XCVII), where the naphthalene ring is fully conjugated with the -CH = C - CO- part of the molecule. The ultraviolet spectrum of the compound, which closely resembled that of a perinaphthenone,




XCVII


24
16
8
ε x10⁻³
2200
2500
3000
λ(Å)
3500
4000
'C20H14O'

provides evidence in favour of this hypothesis.

The loss of $C_6H_5CHOH$-, and $ClC_6H_4CHOH$- is only postulated as an explanation to meet analysis requirements. No parallel elimination has been observed, and it is difficult to conceive a satisfactory mechanism for the removal of this expectedly stable grouping. Since neither the structure of the benzylideneperinaphthanone nor that of its decomposition product has been rigidly established, much of the foregoing is of a hypothetical nature. This aspect of the research is therefore incomplete, and further investigations on the topic must be undertaken to elucidate the products involved in these abnormal reactions.

Attention was turned to the possibility of utilising absorption spectroscopy as a means for orientating phenylmesobenzanthrones. R.N. Jones[75] noted that the ultraviolet absorption spectrum of 1-phenylnaphthalene (resembling a summation of the spectra of napthhalene and benzene) differed markedly from that of 2-phenylnaphthalene, and suggested this difference as being caused by the non-planarity of 1-substituted naphthalenes.

For the phenylmesobenzanthrones, substitution in any of the non-sterically hindered positions 2-, 5-, 10-, and 11-, should result in a planar structure. A biphenyl-type resonance would thus be permitted, and

the spectra of such compounds, by Jones' prediction, would differ from that of the unsubstituted ketone.

Further, phenyl substitution in the sterically hindered positions 1-, 3-, 4-, 6-, 8-, and 11-, would prevent the resultant molecule assuming a planar form. The consequent absence of ring interaction (biphenyl resonance) decrees that compounds so substituted must possess a spectrum similar to that of the parent ketone.

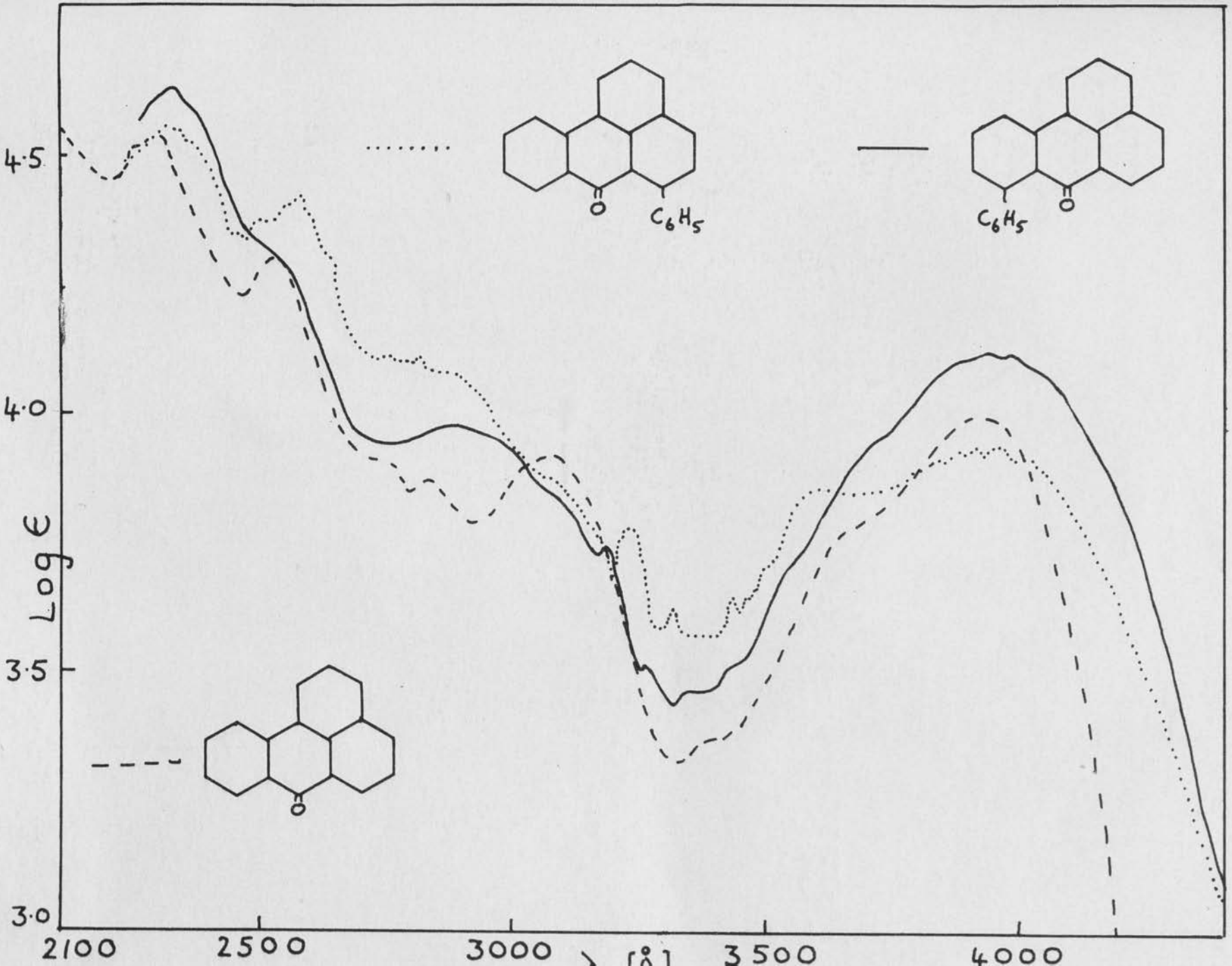
Such predictions have already been verified for 6- and 8-phenylmesobenzanthrone.(37) The present research has extended this to the spectra of the 2- and 3-phenyl derivatives.

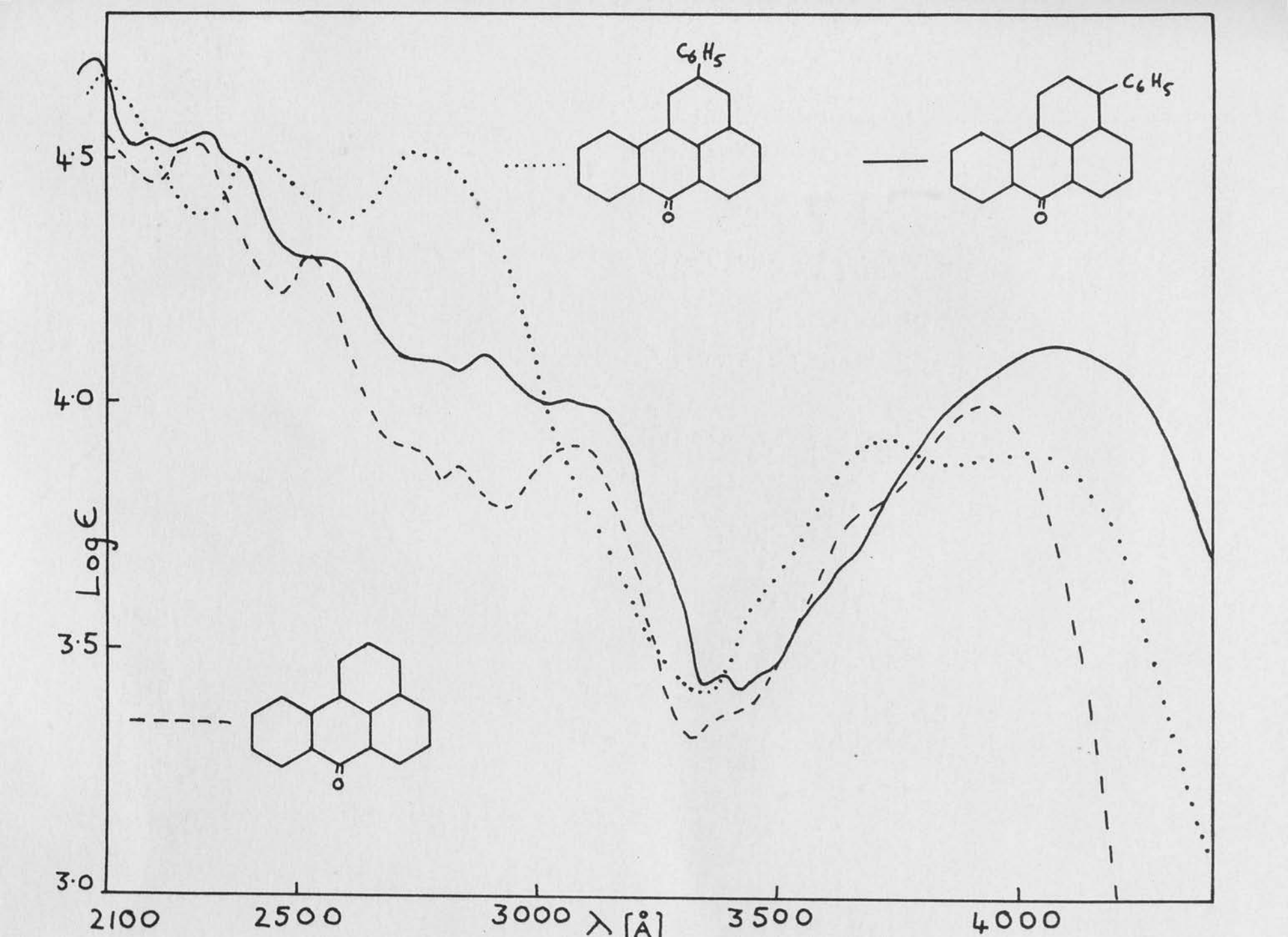
In the former case, a degree of departure from the mesobenzanthrone spectrum is observed, although the difference is not as striking as might be expected. The presence of a double peak ( $\lambda$ max. 4030, 3700A; logs $\epsilon$ = 3.92, 3.95) where previously only a single one existed ( $\lambda$ max. 4070A; log $\epsilon$ = 4.15), lack of fine structure at the 3390A minima, and more pronounced maxima at 2750A (log $\epsilon$ = 4.54) and 2430A (log $\epsilon$ = 4.53) are the only marked differences displayed by 2-phenylmesobenzanthrone.

At the same time, the spectrum of the 3-phenyl isomer bears a strong resemblance to that of mesobenzanthrone.

This evidence as presented is, of necessity, incomplete, and further work will require to be

performed before an overall picture of the effect of phenyl substitution presents itself. None the less, the results obtained from spectroscopic data may be of considerable value when applied to cases where information given by melting point and degradation is ambiguous.


4·5
4·0
3·5
3·0
Log ε
2100
2500
3000
3500
4000
λ [Å]
C6H5
C6H5
O
O
O


C6H5
C6H5
4·5
4·0
3·5
3·0
Log ε
2100
2500
3000
λ [Å]
3500
4000

## EXPERIMENTAL

### The Attempted Synthesis of 8-phenylmesobenzanthrone

#### 1. The Bally-Scholl Synthesis

##### Trans 1-phenylbutadiene

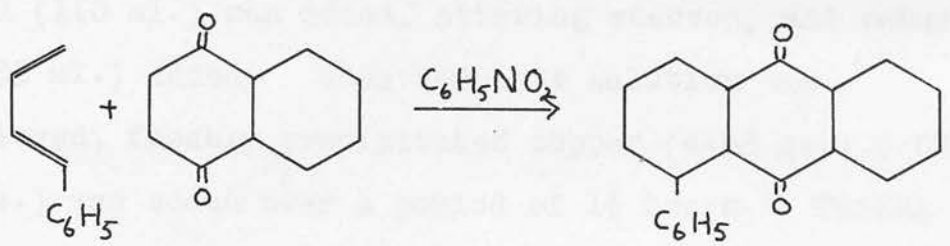
Ref. Organic Syntheses XXX - 75.

$$C_6H_5CH = CH\text{-}CHO \xrightarrow[2.\ H_2SO_4]{1.\ CH_3MgBr} C_6H_5\text{-}CH = CH\text{-}CH = CH_2$$

Yield = 45 gm. (69%). B.Pt. 79-84°C (11-12 mm.).

##### 1-phenylanthraquinone

Ref. Bergman et al, J. Org. Chem. 7, 303, 1942.

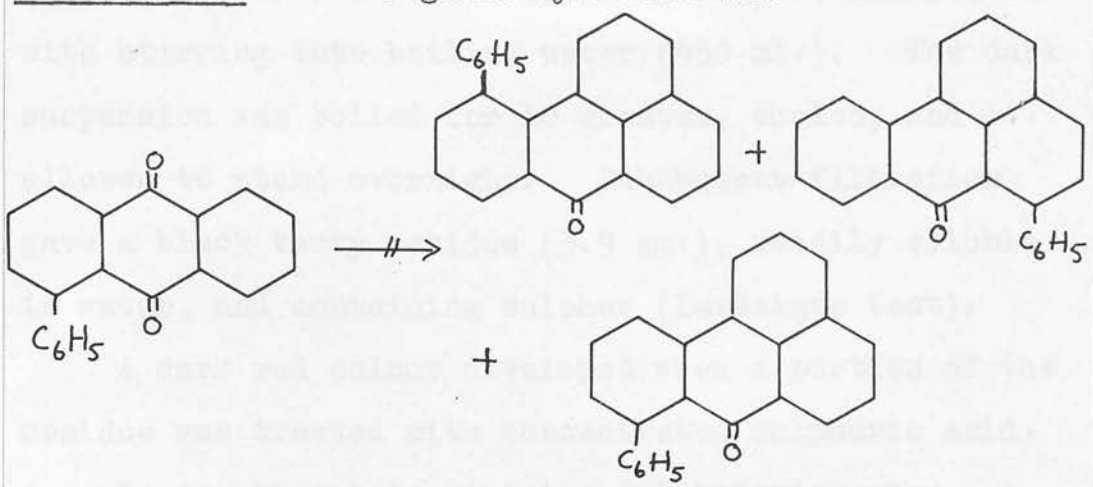



Trans-1-phenylbutadiene (13.0 gm.; 0.1 mole.), 1:4 naphthaquinone (14.2 gm.; 0.09 mole.) and nitrobenzene (12 ml.) were heated in an oil bath at 180°C for 5 minutes. Methyl alcohol (15 ml.) was added, and the product separated out on cooling.

Two recrystallisations from glacial acetic acid (with carbon screening) gave the pure quinone as yellow needles.

Yield 13.8 gm. (54%). M.Pt. 176-177°C.

The Attempted Synthesis of 8 (6) (10)-phenylmeso-benzanthrone - cf. Organic Syntheses XIV - 4.




1-phenylanthraquinone (9.95 gm.; 0.035 mole.) was placed in a 250 ml. 3-necked Quickfit flask, equipped with stirrer and thermometer. Concentrated sulphuric acid (110 ml.) was added, stirring started, and water (4.35 ml.) added. When complete solution was achieved, freshly precipitated copper (4.83 gm.; 0.076 mole.) was added over a period of 1½ hours. During this addition, and for a subsequent 4 hours, the internal temperature was maintained between 38-42°C, by means of a water bath. At the end of this period, all the copper had dissolved.

A mixture of commercial anhydrous glycerol (9.6 gm.; 0.104 mole) and water (9.6 ml.; 0.55 mole.) was introduced over 20 minutes, the temperature being allowed to rise to 90°C. The reactants were slowly heated to 120°C during a period of 1½ hours, by means of an oil bath, with a steady temperature rise of 1 degree every 3 minutes.

After maintaining at 118-120°C for a further 3 hours, the mixture was cooled to 90-100°C, and poured with stirring into boiling water (450 ml.). The dark suspension was boiled for 10 minutes, cooled, and allowed to stand overnight. Subsequent filtration gave a black tarry residue (3.9 gm.), readily soluble in water, and containing sulphur (Lassaigne test).

A dark red colour developed when a portion of the residue was treated with concentrated sulphuric acid.

In an attempt to minimise sulphonation, the experiment was repeated, reducing the time of the final heating from 3 hours to 90 minutes and reducing the final temperature from 120°C to 100°C.

Unfortunately no cleaner product was isolated.

The Attempted Desulphonation of the product of the Bally Synthesis

(a) Cf. Organic Syntheses XXXI - 45.

The above material (0.8 gm.) was heated under reflux with 50% sulphuric acid (50 ml.) for six hours. The dark green solution was poured onto chopped ice (50 gm.), and left overnight. No solid deposited, and no material was extracted with organic solvents.

(b) The material (0.9 gm.) was heated under reflux for 1 hour with 60% sulphuric acid (50 ml.) and mercuric sulphate (0.5 gm.). Cooling and pouring onto chopped ice (50 gm.) gave a clear dark brown

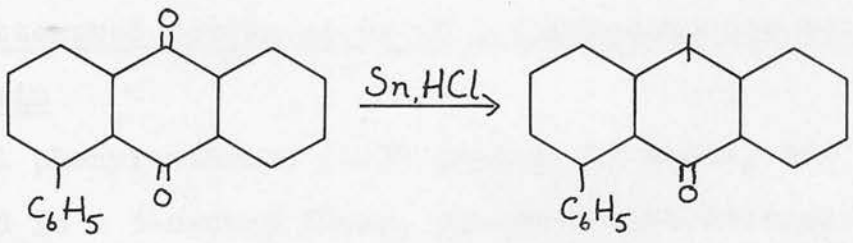
solution, from which no solid could be obtained.

(c) The black solid (0.1 gm.) was dissolved in water (10 ml.) and the solution boiled for 2 hours. No solid material was obtainable on cooling. Removal of solvent left a gummy, unsavoury tar.

Attempted Chromatographic Purification

The black solid (1 gm.) was dissolved in 1:1 xylene:benzene (35 ml.) and chromatographed on an alumina column (14 cm. x 2.5 cm.). Development of the column with 250 ml. 1:1 xylene:benzene separated a narrow pale yellow band from the broad black zone retained at the top of the column. This eluted zone on evaporation gave a brown oil (ca. 20 mg.) which could not be induced to crystallise.

The Reduction of 1 phenylanthraquinone




1 phenylanthraquinone (2.0 gm.; 0.007 mole.), granulated tin (0.7 gm.; 0.006 mole.) and glacial acetic acid (12 ml.) were placed in a 100 ml. quickfit flask, and heated under gentle reflux. To this mixture,

fuming hydrochloric acid (4 ml.) was added over a period of 1½ hours. The yellow solution was boiled for a further hour, and traces of undissolved material removed by hot filtration through a sintered glass filter funnel. The filtrate, on cooling, deposited 1.6 gm. yellow needles, M.Pt. 182-90°C. Recrystallisation from acetic acid, or from 3:1 benzene:light petroleum raised this figure to 194-5°C. A sample of the product admixed with 1 phenylanthraquinone melted over the range 140-180°C.

Yield 1.4 gm. (73.5%).

This material gave a positive Liebermann anthrone test.

Analysis

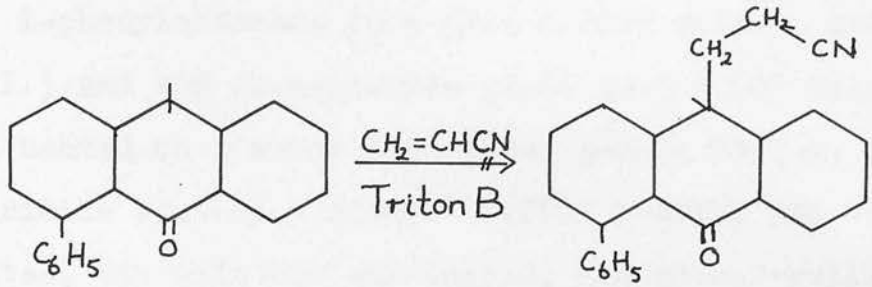
| | | | |
|---|---|---|---|
| | Found | C 86.7% | H 5.4% |
| $C_{20}H_{14}O$ | Requires | C 88.9% | H 5.2% |
| $C_{20}H_{12}O_2$ | Requires | C 84.5% | H 4.2% |

The attempted condensation of 1 phenylanthrone with acrolein

1 phenylanthrone (1.35 gm.; 0.005 mole.) was placed in a 3-necked flask, equipped with stirrer. A mixture of concentrated sulphuric acid (15 ml.) and water (2 ml.) was added, and the suspension stirred. When solution was complete, a mixture of glycerol (1.4 gm.; 0.015 mole.) and water (1.5 ml.) was added over a period of 10 minutes; the temperature at this stage was kept below 90°C. The contents of the flask

were heated to 100°C over a period of 30 minutes, and maintained at this temperature for a further 60 minutes. Working up the reaction in the manner previously described resulted once more in a water soluble sulphonated product.

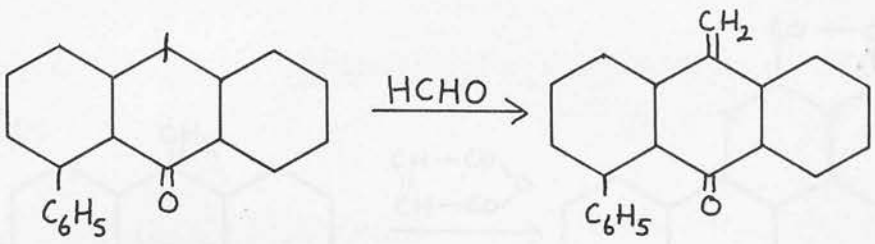
The Attempted monocyanoethylation of 1-phenylanthrone




To a stirred solution of 1 phenylanthrone (2.03 gm.; 0.0075 mole.) and trimethylbenzylammonium hydroxide (1 gm. of 40% aq. solution) in dioxan (15 ml.), acrylonitrile (0.4 gm.; 0.0077 mole.) was added portionwise over 10 minutes. The temperature was maintained at 35-40°C during the addition, and for a subsequent 2 hours. The resulting red solution was allowed to stand at room temperature for 2 days.

Acidification with dilute hydrochloric acid gave a flocculent yellow precipitate, which was filtered off, washed with water, dried on porous tile and re-crystallised from 100/120° light petroleum. A sample melted at 191-193°C, this figure remaining undepressed when the product was admixed with 1-phenylanthrone.

The Condensation of 1-phenylanthrone with formaldehyde



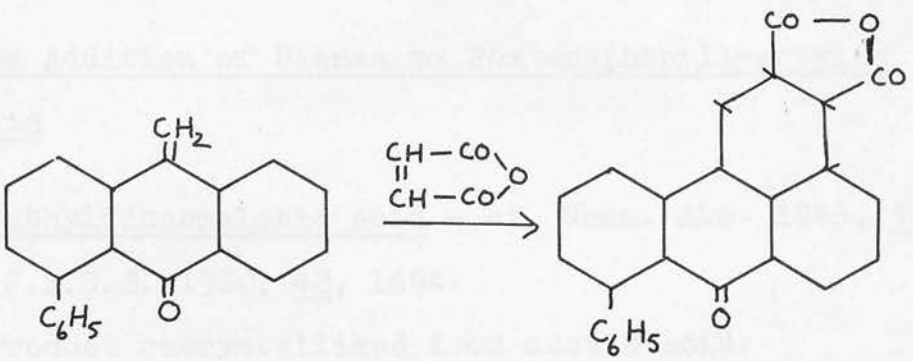

1-phenylanthrone (0.6 gm.; 0.0022 mole.), methanol (6 ml.) and 40% formaldehyde (0.66 gm.; 0.009 mole.) were heated on a water bath under gentle reflux, and piperidine (0.5 ml.) added. After heating for 45 minutes, the solution was cooled, and orange-yellow plates commenced to deposit, together with some light brown gummy material, probably polymeric in nature. The product was filtered off, and recrystallised from aqueous methanol to give yellow plates, M.Pt. 109-110°C. A sample on admixture with 1-phenylanthrone, melted over the range 74-190°C.

Yield 0.4 gm. (64%).

Analysis

| | | | |
|---|---|---|---|
| | Found | C 88.6% | H 5.0% |
| $C_{21}H_{14}O$ | Requires | C 89.4% | H 5.0% |

The Attempted Condensation of 1-phenyl-10-methylene-anthrone with maleic anhydride




1-Phenyl-10-methyleneanthrone (0.28 gm.; 0.001 mole.), maleic anhydride (0.2 gm.; 0.002 mole.) and nitrobenzene (6 ml.) were mixed, and heated under gentle reflux for 1 hour. The mixture was cooled, benzene (10 ml.) added, and nitrobenzene was removed by steam distillation. The residual oil was dissolved in benzene (6 ml.), dried with sodium sulphate, and chromatographed on a column of alumina ($\frac{3}{4}$" x 6"). Eluting with benzene removed a pale yellow zone from the red-brown band at the top of the column. On evaporation of benzene, a small quantity of orange brown material was left as a residue. Crystallisation from aqueous methanol gave light brown needles (2 mgm.), M.Pt. 170-171°C. The compound dissolved in concentrated sulphuric acid to give an orange yellow solution, exhibiting orange fluorescence in ultraviolet light. Further elution of the column with ethyl acetate only produced traces of an oily non-crystalline residue.

In view of the extremely small yield, the synthesis was abandoned.

2. The Addition of Dienes to 2(α -naphthyl)-acrylic acid

α -naphthylidenemalonic acid - cf. Chem. Abs. 1945, 39, 926; J.A.C.S. 1920, 42, 1664.

Product recrystallised from acetic acid.

Yield 38 gm. (82%). M.Pt. 196°C (lit 195-196°C).

2(α -naphthyl)-acrylic acid

α -Naphthylidenemalonic acid (35 gm.) was placed in a conical flask, and heated in an oil bath at 210-220°C. Evolution of carbon dioxide, commencing after 5 minutes, ceased after 30 minutes.

The melt was maintained at 215°C for a further 15 minutes, and allowed to cool. The sublimate and residue were combined, dissolved in 10% sodium carbonate (150 ml.), and coloured impurities largely removed by washing with successive 25 ml. portions of benzene.

After being precipitated by hydrochloric acid, the product was filtered, washed with water, and recrystallised from methylated spirits.

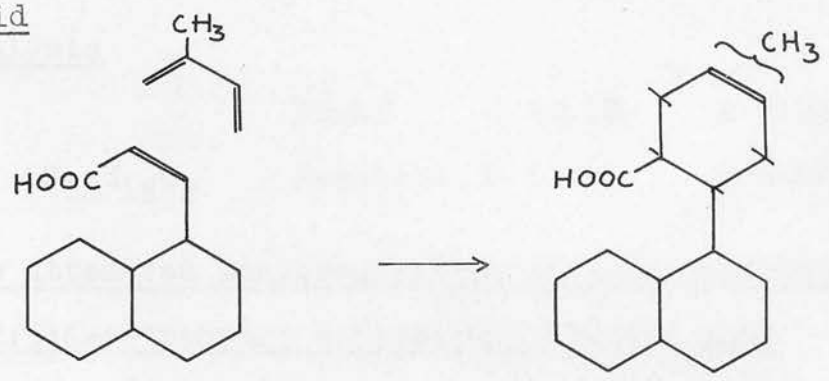
Yield 16 gm. (56%). M.Pt. 209-10°C (lit. 209-212°C).

The ethyl ester was prepared by heating for 6 hours under reflux a mixture of the acid (5.4 gm.), ethanol

(70 ml.), and concentrated sulphuric acid (2 ml.).

Yield 6.1 gm. (Quantitative). M.Pt. 37-38°C (lit. 37.5°C).

A. The Addition of Isoprene to 2-(α-naphthyl)-acrylic acid




2-(α-Naphthyl)-acrylic acid (2.5 gm.), isoprene (12 ml.), and redistilled sulphur-free xylene (20 ml.) were heated in a sealed Carius tube at 180°C for 24 hours. The resulting pale yellow solution was diluted with ligroin (25 ml.) and extracted with 10% sodium carbonate (3 x 20 ml.). The combined extracts, after washing with ether (20 ml.), were acidified with 2N HCl, and the free acid extracted with ether (30 ml.). The ether layer was washed with water and dried with sodium sulphate. Removal of solvent left a pale yellow viscous oil, which, on standing in Drikold/acetone deposited white grains (1.2 gm.), M.Pt. 130-132°C, with some softening observed at 86-90°C. Crystallisation from 100/120° light petroleum gave a product melting sharply at

132-133°C.

Yield 1.1 gm. (33%).

A sample dissolved in warm concentrated sulphuric acid to give a dark red colour with green fluorescence.

Analysis

| | | | |
|---|---|---|---|
| | Found | C 80.1% | H 7.2% |
| $C_{18}H_{18}O_2$ | Requires | C 81.2% | H 6.8% |

The Attempted Dehydrogenation of 2-(α-naphthyl) 1:2:3:6-tetrahydro 4(5)-methyl benzoic acid

(a) The acid (100 mg.) was dissolved in warm nitrobenzene (25 ml.) and heated under reflux for 4 hours. The dark brown solution was cooled, diluted with benzene (30 ml.) and extracted with 10% sodium carbonate solution. The extract was washed with ether, and acidified with hydrochloric acid. The white precipitate was recrystallised from light petroleum to yield 60 mgm. of product, M.Pt. 132-133°C, undepressed on admixture with starting material.

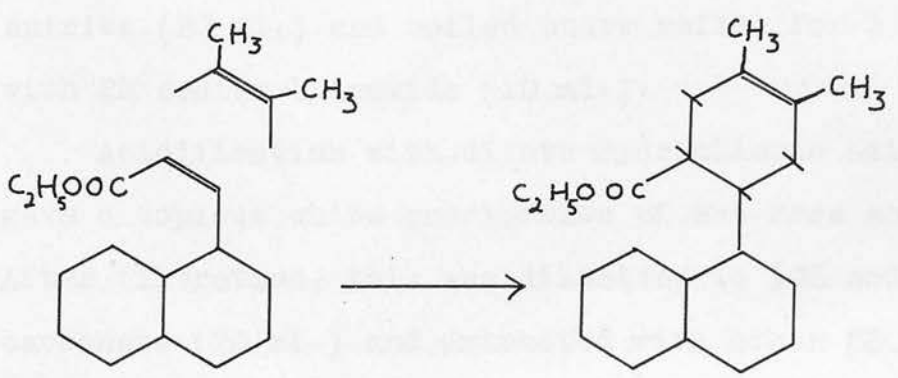
(b) The acid (150 mg.) and chloranil (250 mg.) were dissolved in sulphur-free xylene (15 ml.) and boiled under gentle reflux for 24 hours. The resulting brown solution was extracted with 10% sodium bicarbonate (10 ml.) which, when acidified, yielded no precipitate. Further extractions with sodium carbonate, and with

sodium hydroxide furnished no acidic material. Evaporation of the xylene solution gave a dark brown gum, which resisted attempts at recrystallisation.

The Attempted Cyclisation of 2-(α -naphthyl)-1:2:3:6 tetrahydro 4(5)-methyl benzoic acid

The above acid (400 mg.) was dissolved in concentrated sulphuric acid (5 ml.) and heated on a water bath at 50°C for 1 hour. The dark red solution was poured into cold water (100 ml.), yielding a deep yellow solution showing faint green fluorescence. Extractions with ether, ethylacetate, benzene, xylene, and chloroform failed to produce any material. Sodium carbonate (10 gm.) was added to the aqueous solution which was reduced in volume until sodium sulphate began to precipitate. Extraction at this stage once more proved unfruitful, and the cyclisation was abandoned.

B. The Condensation of 2:3-dimethylbutadiene with ethyl 2(-α -naphthyl)-acrylate



The ester (5 gm.; 0.025 mole.), 2,3-dimethylbutadiene (9 gm.; 0.11 mole.) and sulphur-free xylene (10 ml.) were heated together in a sealed Carius tube at 185°C for 40 hours. Traces of carbonaceous material were removed by filtration, and the light brown solution fractionated, three fractions being collected.

Fraction 1. B.Pt. 136-140°C (760 mm.) - xylene forerun.

Fraction 2. B.Pt. 100-104°C (25 mm.) - probably the dimer of 2:3-dimethylbutadiene, B.Pt. 180°C, 2.5 gm.

Fraction 3. B.Pt. 148-150°C (0.1 mm.) - pale yellow oil. 4.4 gm.

Analysis of Fraction 3:

| | | | |
|---|---|---|---|
| | Found | C 81.7% | H 8.1% |
| $C_{21}H_{24}O_2$ | Requires | C 81.8% | H 7.9% |

Yield 64%.

The Hydrolysis of ethyl 2-(α-naphthyl)-4:5-dimethyl-1:2:3:6-tetrahydro benzoate

The ester (1.5 gm.) was dissolved in methylated spirits (20 ml.) and boiled under reflux for 1 hour with 2N sodium hydroxide (10 ml.).

Acidification with dilute hydrochloric acid gave a copious white precipitate of the free acid. After filtration, this was dissolved in 10% sodium carbonate (20 ml.) and extracted with ether (2 x 10

ml.) to remove traces of a gummy component. Reprecipitation, and recrystallisation from alcohol or light petroleum gave the pure acid as cubic prisms, M.Pt. 158-9°C, which were soluble in acetic acid and benzene.

Yield 1.1 gm. (81%).

| | | | |
|---|---|---|---|
| Analysis | Found | C 81.0% | H 7.0% |
| $C_{19}H_{20}O_2$ | Requires | C 81.4% | H 7.1% |

The Attempted Dehydrogenation of 2-(α-naphthyl)-4:5-dimethyl-1:2:3:6-tetrahydro benzoic acid

The acid (300 mg.) was dissolved in sulphur-free xylene (25 ml.); chloranil (500 mg.) was added, and the mixture heated under reflux for 24 hours. The dark brown solution was cooled, filtered to remove traces of undissolved material and extracted with 10% sodium bicarbonate solution (3 x 10 ml.), from which unchanged starting material was recovered on acidification. Concentration of the organic phase gave a precipitate of chloranil.

The Attempted Cyclisation of 2-(α-naphthyl)-4:5-dimethyl-1:2:3:6-tetrahydro benzoic acid

(a) A mixture of the acid (200 mg.) and polyphosphoric acid (50 gm.) was heated on an oil bath at 140°C for 20 minutes. The resulting dark red solution which exhibited green fluorescence was cooled, poured into water, and the dark

green aqueous phase extracted with ether. A back extraction with sodium carbonate showed the absence of unreacted acid. Removal of ether left a brown oil, which deposited brown needles (ca. 3 mgm.) on standing overnight. Recrystallisation from acetic acid, with the addition of animal charcoal, gave yellow brown needles, M.Pt. 148-153°C, in quantity too small for analysis.

(b) The acid (200 mg.) was dissolved in concentrated sulphuric acid (10 ml.), and the resulting red solution was maintained for 1 hour at 45-50°C. Pouring into water furnished a green solution from which no organic material could be extracted.

(c) A mixture of the acid (150 mg.) and thionyl chloride (5 ml.) was heated under reflux for 30 minutes. Excess thionyl chloride was distilled off, and carbon disulphide (15 ml.) added, followed by powdered aluminium chloride (100 mg.). The mixture was heated under reflux for a further three hours, cooled, and decomposed with ice water. Ether extraction yielded traces of an amorphous brown solid possessing an indefinite melting point, and giving a red solution (green fluorescing) in sulphuric acid.

C. The Attempted Condensation of 1-phenylbutadiene with 2-(α-naphthyl)-acrylic acid

I. Naphthylacrylic acid (2 gm.; 0.01 mole.), 1-phenyl butadiene (2 gm.; 0.014 mole.) and nitrobenzene (8 ml.) were heated on a boiling water bath for 15 hours. Extraction of the solution with 10% sodium carbonate, and subsequent acidification of the extract gave 2.1 gm. of a white solid, which crystallised from aqueous alcohol as colourless needles, M.Pt. 208-209°C, undepressed on admixture with 2-(α-naphthyl)-acrylic acid.

II. The reactants were mixed in the above proportions and heated for 30 minutes in an oil bath, maintained at 175-180°C. Unchanged starting material was recovered in 95% yield.

III. The reaction was carried out on the above scale in a sealed Carius tube, the heating being maintained at 150°C for 17 hours, followed by a final 50 hours at 190°C. A 70% recovery of starting material was effected.

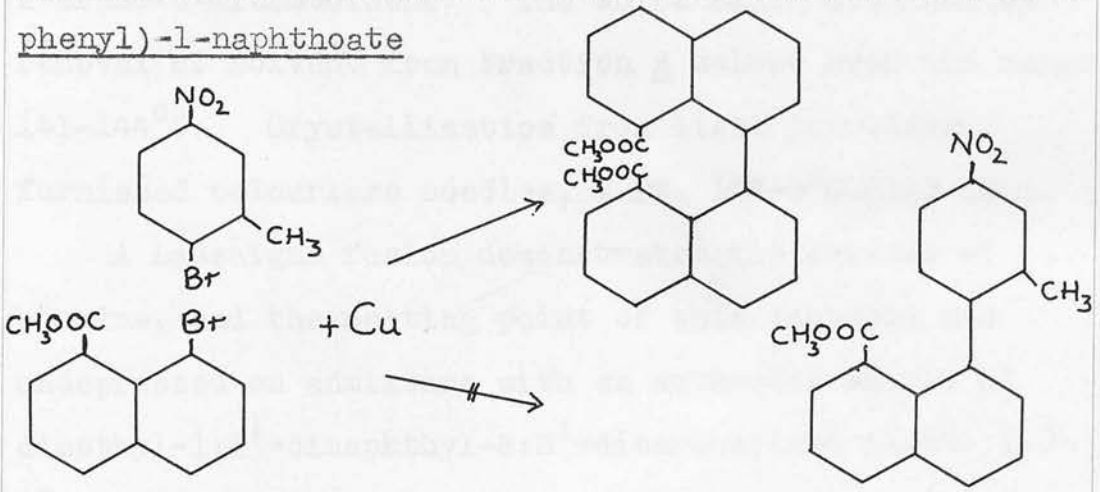
IV. Repeating III with the substitution of sulphur-free xylene for nitrobenzene yielded similar results.

The Ullmann Reaction

Methyl 8-bromo-1-naphthoate was prepared in 80% yield by esterification of 8-Bromo-1-naphthoic acid (F.R. Smith, Thesis, Edinburgh).

2-Bromo-5-nitrotoluene was prepared from 2-amino-5-nitrotoluene by the method of Gibson and Johnston (J.C.S. 1929, 1244). Two recrystallisations from alcohol gave the pure product, M.Pt. 75-76°C.

The Attempted Preparation of methyl-8(2-methyl-4-nitrophenyl)-1-naphthoate




A mixture of methyl-8-bromo-1-naphthoate (2 gm.; 0.075 mole.) and 2-bromo-5-nitro-toluene (3.2 gm.; 0.15 mole.) was heated for 2 hours in an oil bath maintained at 180°C. Copper bronze (4 gm.) was added portionwise during the first 20 minutes.

The melt was cooled, and extracted with ether (10 ml.), ethyl acetate (20 ml.), and acetone (20 ml.). Removal of solvent left a brown white residue, which was dissolved in 2: 1 benzene/60-80° light petroleum, and chromatographed on a column of alumina (25 cm. x 2 cm.).

With 1:1 benzene/petroleum as eluent, an orange zone, A, was washed through rapidly, leaving a dark brown layer at the top of the column.

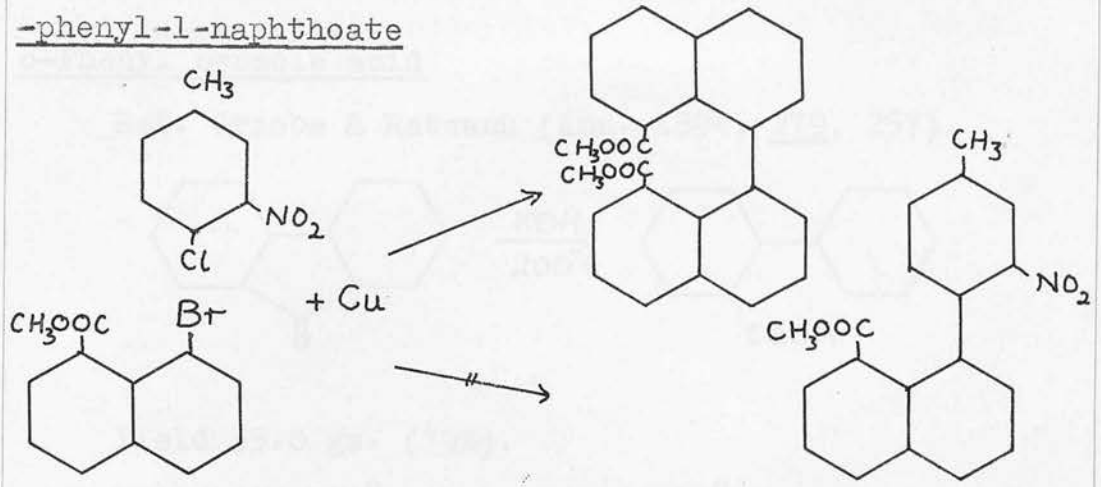
Further development of the column with pure benzene (150 ml.) removed a zone, B, which showed a faint blue fluorescence in ultraviolet light.

Concentration of Fraction A caused the deposition of orange yellow granules, (2.7 gm.), which was shown by melting-point and mixed melting-point to be unchanged 2-Bromo-5-nitrotoluene. The white solid obtained by removal of solvent from Fraction B melted over the range 141-144°C. Crystallisation from light petroleum furnished colourless needles, M.Pt. 144-5°C (1-2 gm.).

A Lassaigne fusion demonstrated the absence of bromine, and the melting point of this compound was undepressed on admixture with an authentic sample of dimethyl-1:1'-dinaphthyl-8:8'-dicarboxylate (M.Pt. 142-3°C). Yield 86%.

Repetition of the condensation employing quantities of up to 400% excess of the nitrobromotoluene gave similar results.

The Attempted Preparation of methyl-8-(2-nitro-4-methyl)-phenyl-1-naphthoate




Methyl-8-bromonaphthoate (6.2 gm.; 0.023 mole.), 4-chloro-3-nitrotoluene (7.5 gm.; 0.047 mole.) and copper bronze (12 gm.) were heated for 2 hours at 180-190°C.

Extraction with acetone and ether gave yellow solutions; concentration of the combined extracts gave a yellow oil, which distilled under reduced pressure to give a pale yellow liquid (6.5 gm.) containing chlorine, B.Pt. 130°C (16 mm.). (Cf. B.Pt. of 4-chloro-3-nitrotoluene 118°C (11 mm.))

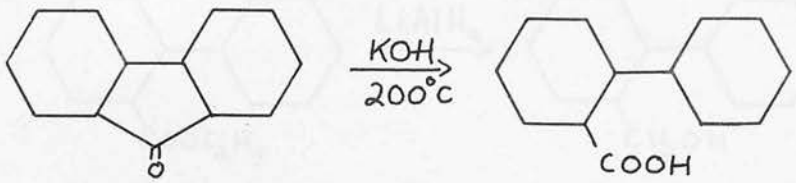
The light brown residue from the distillation, when recrystallised from 100-120° ligroin gave dimethyl 1:1'-dinaphthyl-8:8'-dicarboxylate (3.8 gm., 88%) identified by melting point and mixed melting point.

Further modifications in the molar quantities employed did not result in the isolation of any of the asymmetric product.

A. The Synthesis of 1(o-phenyl-benzyl)-naphthalene

o-Phenyl benzoic acid

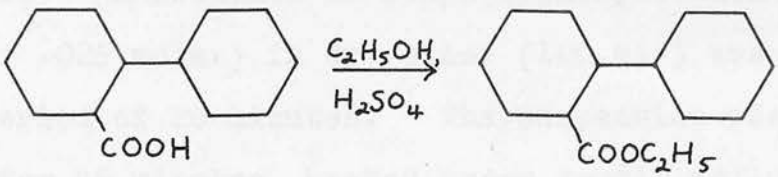
Ref. Graebe & Rateanu (Ann. 1894, 279, 257).




Yield 35.0 gm. (79%).

M.Pt. 113-114°C (lit. M.Pt. 114°C).

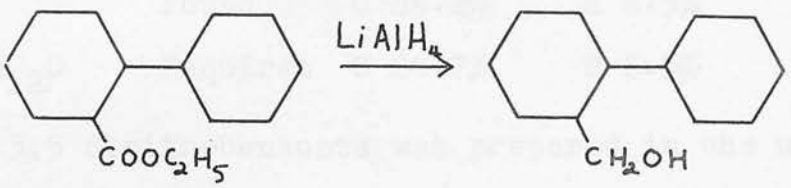
Ethyl o-phenyl-benzoate - (cf. Wang, Thesis, Edinburgh University)




o-Phenylbenzoic acid (15 gm.; 0.075 mole.), ethyl alcohol (45 ml.) and concentrated sulphuric acid (1 ml.) were heated under gentle reflux for 8 hours. Excess alcohol was removed by distillation, the residual oil was poured into water (100 ml.), and back extracted into ether (50 ml.). After washing with successive portions of 10% sodium carbonate and water, a fractional distillation yielded the ester. B.Pt. 176-179°C (16 mm.). Lit. 163-166°C (12 mm.).

Yield 12.8 gm., 74%.

The preparation of o-phenylbenzyl alcohol - (cf. St. Goldschmidt & Veer, Rec. Trav. Chim. 1948, 67; 489).




A suspension of Lithium Aluminium hydride (1.0 gm.; 0.026 mole.) in dry ether (75 ml.) was placed in a dry 250 ml. 3-necked flask equipped with mercury sealed stirrer and a condenser fitted with a calcium chloride guard tube. A solution of ethyl-o-phenylbenzoate (6.0 gm.; .026 mole.) in dry ether (100 ml.) was added over a period of 20 minutes. The suspension was stirred for 45 minutes, heated under gentle reflux for a further 30 minutes, and left overnight. Excess Lithium Aluminium Hydride was decomposed by the cautious addition of ethyl acetate (25 ml.), and the mixture poured into chopped ice (100 gm.) containing 2N sulphuric acid (25 ml.).

The two layers were separated, and the ether layer washed with successive 10 ml. portions of 10% sodium carbonate, and water. The solution was dried overnight with sodium sulphate, ether was removed, and the alcohol distilled under reduced pressure, as a colourless oil, B.Pt. 175-177°C (9 mm.), which later solidified to give white needles, M.Pt. 41-42°C. Lit.

B.Pt. of o-phenylbenzyl alcohol 174° (13 mm.).

Yield 4.4 gm. (90.2%).

Analysis

| | | | |
|---|---|---|---|
| | Found | C 86.2% | H 6.5% |
| $C_{13}H_{12}O$ | Requires | C 84.7% | H 6.5% |

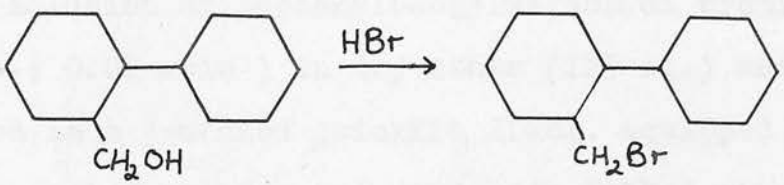
The 3,5 dinitrobenzoate was prepared in the usual manner. Recrystallisation from alcohol gave colourless elongated prisms. M.Pt. 129-130°C.

Analysis

| | | | | |
|---|---|---|---|---|
| | Found | C 65.3% | H 4.2% | N 7.5% |
| $C_{20}H_{14}O_6N_2$ | Requires | C 63.5% | H 3.7% | N 7.4% |

It was found possible to prepare the alcohol in 88% yield by reduction of o-phenyl-benzoic acid with Lithium Aluminium Hydride.

o-Phenylbenzyl bromide




o-Phenylbenzyl alcohol (6.0 gm.; 0.033 mole.) in ether (20 ml.) was added to a solution of hydrogen bromide (7.0 gm.) in ether (200 ml.).

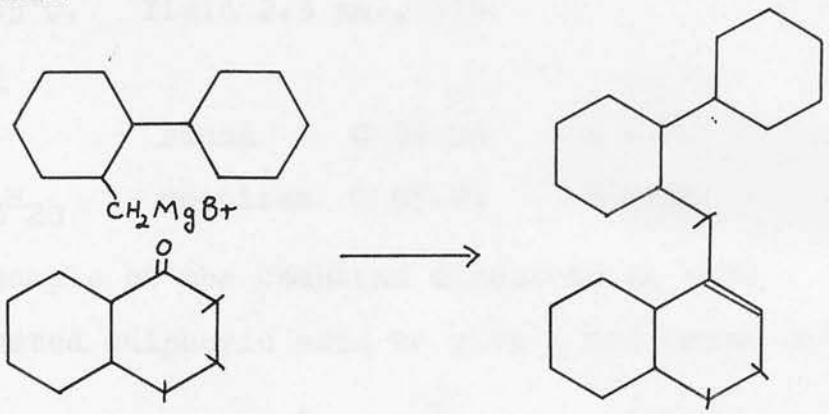
The solution was kept for 2 days with occasional swirling, at the end of which time a separation into 2 layers had occurred. The lower orange brown layer was discarded, and the upper layer washed with 20% sodium carbonate (2 x 20 ml.) and with water (20 ml.).

After drying overnight with sodium sulphate, ether was removed, and o-phenylbenzyl bromide collected by distillation under reduced pressure.

Yield 6.5 gm. (80.7%). B.Pt. 158-160°C (8 mm.). (Lit. B.Pt. 161°C (11 mm.))

This compound was found to be extremely lachrymatory.

The Preparation of 3:4-dihydro-1-(-2'-phenylbenzyl) naphthalene




A solution of o-phenylbenzylmagnesium bromide (5.5 gm.; 0.02 mole.) in dry ether (125 ml.) was prepared in a 3-necked quickfit flask, equipped with a mercury sealed stirrer and condenser fitted with a calcium chloride guard tube. To this solution was added, with stirring, a solution of tetralone (redistilled, 3.0 gm.; 0.02 mole.) in dry ether (40 ml.). Throughout the addition, which took 30 minutes, the temperature was maintained between 0-5°C, and a stream of dry nitrogen passed through the flask. After stirring for a further 45 minutes, the solution was

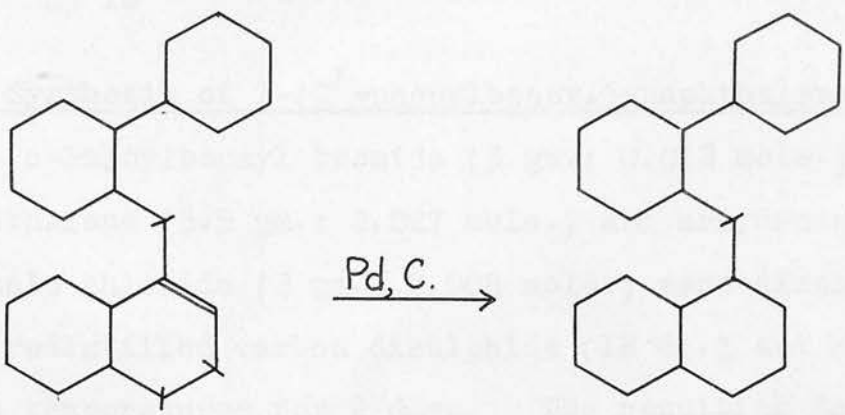
poured into a mixture of 2N hydrochloric acid (15 ml.) and finely chopped ice (80 gm.). The ether layer was separated, washed successively with 10% sodium bicarbonate (25 ml.) and water (25 ml.) and dried overnight with sodium sulphate. Removal of solvent left a light brown oil, which when triturated with ice cold ethyl acetate (1 ml.) yielded "off white" crystals, M.Pt. 109-112°C. When recrystallised from alcohol, the compound was obtained as colourless needles, M.Pt. 112-112.5°C. Yield 2.3 gm., 37%.

Analysis

| | | | |
|---|---|---|---|
| | Found | C 92.5% | H 6.6% |
| $C_{23}H_{20}$ | Requires | C 93.2% | H 6.8% |

A sample of the compound dissolved in warm concentrated sulphuric acid to give a red brown colour.

The Preparation of 1-(2'-phenylbenzyl)-naphthalene. A.




A test tube containing an intimate mixture of 3:4-dihydro-1-(2'-phenylbenzyl)-naphthalene (0.6 gm.; 0.002 mole.) and 30% palladium charcoal catalyst (0.2 gm.) was heated at 150°C in a Wood's metal bath,

for 3 hours, with a slow current of dry carbon dioxide passing through the test tube. During this period of heating a sublimation of colourless needles took place on the cooler part of the test tube. The test tube was allowed to cool, and its contents extracted with ether (2 x 10 ml.). A white solid (M.Pt. 117-121°C) was obtained on allowing the ether to evaporate. (This solid was insoluble in cold concentrated sulphuric acid; on warming, a colourless solution resulted.) The solid was readily soluble in cold benzene and petrol ether. Recrystallisation from glacial acetic acid gave colourless needles, M.Pt. 121-122°C. A sample on admixture with the dihydro compound melted over the range 85-111°C.

Yield 0.48 gm. (80%).

Analysis

| | | | |
|---|---|---|---|
| | Found | C 93.4% | H 6.5% |
| $C_{23}H_{18}$ | Requires | C 93.8% | H 6.2% |

The Synthesis of 1-(2'-phenylbenzyl)-naphthalene. B.

o-Phenylbenzyl bromide (3 gm.; 0.012 mole.), naphthalene (3.5 gm.; 0.027 mole.) and anhydrous stannic chloride (2 gm.; 0.008 mole.) were dissolved in dry redistilled carbon disulphide (18 ml.) and kept at room temperatures for 2 days. The resulting dark brown solution was heated under gentle reflux for six hours on a water bath, and decomposed by pouring into ice-water (200 ml.). The mixture was extracted with ether (2 x 25 ml.) and benzene (1 x 25 ml.). The

extracts were combined, concentrated to 20 ml., and steam distilled. Naphthalene (2.4 gm.; 0.019 mole.) was obtained from the distillate.

The residual material from the distillation consisted of brown nodules, which coalesced on standing to give a tacky solid. This was dissolved in benzene (15 ml.) and chromatographed on alumina (10 cm. x 1.5 cm.). On elution with benzene, a brown syrup (1.7 gm.) was ultimately obtained. Fractionation of this yielded a pale yellow viscous oil 0.9 gm., B.Pt. 148-150°C (0.1 mm.) , which solidified overnight, yielding an "off white" crystalline solid, M.Pt. 73-95°C. This contained no labile bromine, and dissolved in warm concentrated sulphuric acid, giving a pale yellow solution. A sample gave a red colour when treated with benzal chloride.

The solid was dissolved in 1:1-benzene/light petroleum (15 ml.) and chromatographed on alumina (15 cm. x 1.5 cm.). Light petroleum (60-80°C) was used as eluent, and six separate 20 ml. fractions were collected. The first three such fractions yielded a further crop of naphthalene (0.15 gm.). Fractions 4 and 5 yielded an "off white" solid (0.08 gm.), M.Pt. 77-99°C.

Fraction 6, on concentration, furnished a white solid (0.07 gm.), M.Pt. 114-119°C. Colourless needles (0.05 gm.) were obtained on recrystallisation from acetic acid, M.Pt. 119-120°C.

A sample on admixture with the compound prepared by the dehydrogenation of 3:4 dihydro-1-(2'-phenylbenzyl)-naphthalene melted at 118-120°C.

Analysis

| | | | |
|---|---|---|---|
| | Found | C 93.7% | H 6.2% |
| $C_{23}H_{18}$ | Requires | C 93.8% | H 6.2% |

The Attempted Synthesis of 1-(2'-phenylbenzoyl)-naphthalene

o-Phenyl-benzoic acid (2.0 gm.; 0.001 mole.) was added to thionyl chloride (6.0 gm.) in a flask protected by a calcium chloride tube. After leaving for a day with occasional shaking, excess thionyl chloride was removed by distillation in vacuo; the yellow liquid was dissolved in dry carbon disulphide (10 ml.). Naphthalene (1.3 gm.; 0.01 mole.) was added portionwise, followed by powdered aluminium chloride (1.5 gm.; 0.011 mole.). The mixture rapidly darkened, and was allowed to stand at room temperature overnight. The black solution was warmed for 30 minutes, cooled, and the complex decomposed by pouring on to ice water (150 gm.). The brown solid was filtered off, and boiled with successive 20 ml. portions of 2N hydrochloric acid and water. The solid remaining after filtration was steam distilled, a quantitative recovery of naphthalene being isolated from the distillate. The dark yellow residue from the distillation was dried in vacuo, and re-crystallised from benzene, with carbon screening, to

give yellow needles, M.Pt. 83-84°C, undepressed when mixed with a sample of pure fluorenone. Yield 1.4 gm. (78%).

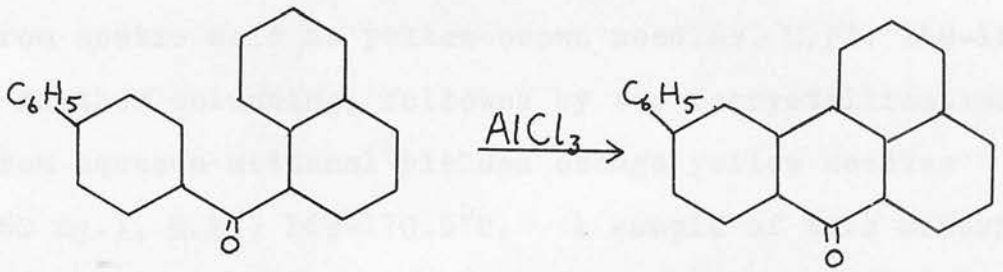
The Synthesis of 10-phenylbenzanthrone

1-(4'-phenylbenzoyl)-naphthalene

Ref. Scholl and Seer, Ann. 1912, 394, 145.

The product crystallised from glacial acetic acid as colourless leaflets. M.Pt. 136-7°C. Yield 9.7 gm. (73%).

The Intramolecular Cyclisation of 1-(4'-phenylbenzoyl)-naphthalene - cf. Scholl and Seer (loc. cit.).



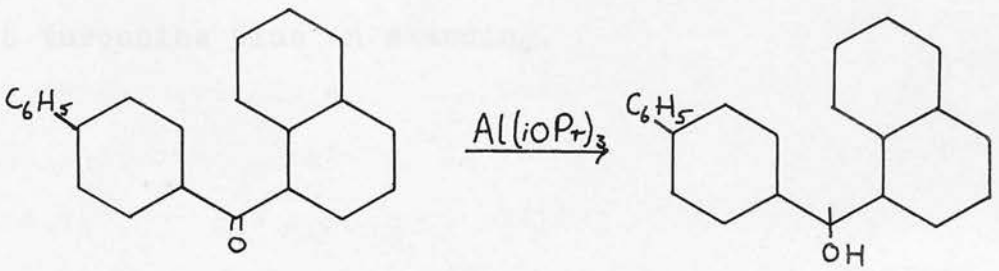

A powdered mixture of aluminium chloride (8 gm.) and 1-(4'-phenylbenzoyl)-naphthalene were fused for 3 hours at 140-145°C, and decomposed according to the above authors. The dark brown residue was dissolved in boiling acetic acid (15 ml.) and screened with carbon. Dilution of the cooled solution with water gave a yellow flocculent precipitate, which was filtered off and dried in a steam oven. Successive recrystallisations from

(a) aqueous alcohol, and (b) pyridine yielded yellow brown imperfect crystals (0.9 gm.), M.Pt. 156-163°C. This melting point remained unsharp after further recrystallisations from alcohol and from acetic acid.

The solid (0.8 gm.) was dissolved in benzene (10 ml.), and chromatographed on a column of alumina (20 cm. x 2 cm.). Using benzene as the eluent, the main fraction washed through rapidly as a yellow band, leaving a broad brown zone at the top of the column. This latter zone was eluted with ether, a brown oil (100 mg.) being obtained on removing the solvent.

Attempts to induce this oil to crystallise were unsuccessful. The main fraction, on concentration, yielded a brown residue (400 mg.) which crystallised from acetic acid as yellow-brown needles, M.Pt. 158-163°C. A further columning, followed by two recrystallisations from aqueous methanol yielded orange yellow needles (60 mg.), M.Pt. 169-170.5°C. A sample of this material when admixed with mesobenzanthrone melted over the range 130-168°C.

<u>The Aluminium iso propoxide reduction of 1-(4'-phenylbenzoyl)-naphthalene</u>



1-(4'-phenylbenzoyl)-naphthalene (1 gm.) was heated under gentle reflux for 17 hours with an anhydrous solution of aluminium iso propoxide prepared from aluminium turnings (0.75 gm.) and dry, redistilled iso propanol (50 ml.). A Hahn partial reflux condenser was then fitted, and 25 ml. of solvent distilled off over a period of 1½ hours, using methanol as the coolant. The presence of acetone in the distillate was confirmed by D.N.P. reagent.

The solution was boiled under gentle reflux for a further hour, and the solvent removed. The residual oil on treatment with 2N sulphuric acid (15 ml.) gave a white precipitate, which was extracted with successive portions of ether (10 ml.) and benzene (10 ml.).

These extracts were combined, washed with 10% sodium carbonate solution (15 ml.) and with water (2 x 10 ml.), and dried with sodium sulphate. Removal of solvent yielded a white residue (0.95 gm.) which crystallised from methanol or 100-120°C petroleum as colourless needles, M.Pt. 125-6°C. Mixed M.Pt. with starting material 105-126°C. Yield 0.85 gm. (84.5%).

A sample of the product dissolved in concentrated sulphuric acid to give a dark green solution, turning to turquoise blue on standing.

Analysis

| | | | |
|---|---|---|---|
| | Found | C 88.7% | H 5.8% |
| $C_{23}H_{17}O$ | Requires | C 89.0% | H 5.8% |
| $C_{23}H_{17}$ | Requires | C 93.8% | H 6.2% |
| Starting material | Requires | C 89.5% | H 5.2% |

The Michael Reaction

Perinaphthanone

(Cf. Fieser and Gates, J.A.C.S. 1940, 62; 2335.)

2-(α-naphthyl)-propionic acid (46 gm., prepared from naphthalene in 4 stages as described by the above authors) was placed in a polythene beaker and dissolved in anhydrous hydrogen fluoride. After allowing to stand in a well ventilated atmosphere for 2 hours, the red solution was poured onto cracked ice (350 gm.). The pale yellow precipitate so formed was removed by filtration, dissolved in benzene (250 ml.), and washed with 10% sodium carbonate; from these washings a total of 13.4 gm. of acid was recovered.

The benzene extract was washed with water, concentrated to 60 ml., and diluted to 100 ml. with ether. The resulting solution was chromatographed without extensive decomposition on the column. Elution with 1:1 benzene/ether (600 ml.) gave on evaporation of solvent 21 gm. (70%) of ketone, M.Pt. 76-79°C. A sample crystallised from light petroleum melted over the range 81-82°C (lit. 82.5-83°C) and

readily formed the oxime, M.Pt. 125-6°C (lit. 125-6°C). Later fractions off the column yielded solid (2.1 gm.), M.Pt. 73-119°C, probably a mixture of the above ketone, and the isomeric cyclisation product, 4:5 benzhydrindone.

The Interaction of Benzaldehyde with Perinaphthanone

1. Perinaphthanone (0.2 gm., $1.1 \times 10^{-3}$ mole) was dissolved in alcohol (5 ml.) and potassium hydroxide pellets (0.2 gm.) were added with shaking until solution was achieved. The solution was allowed to stand for a day, the colour slowly turning to dark brown. The supernatant liquor was decanted from traces of a carbonaceous residue, and diluted with water (10 ml.). Acidification with dilute hydrochloric acid precipitated reddish-brown amorphous material, M.Pt. 57-59°C). This was extracted with successive portions of hot benzene (4 x 10 ml.), and the pale yellow extract concentrated and diluted with petrol. On cooling, perinaphthanone separated out.

   Yield = 0.09 gm. (45% recovery).

2. Perinaphthanone (1.0 gm.; $5.5 \times 10^{-3}$ mole) was dissolved in 4% alcoholic KOH (10 ml.) and redistilled benzaldehyde (3.5 gm.; $3.2 \times 10^{-2}$ mole) added. The solution rapidly darkened, and yellow crystals separated after 5 hours. After leaving overnight, the solid was filtered off, dissolved in ether/benzene (40 ml.), washed with successive

20 ml. portions of 10% sodium carbonate solution, dilute hydrochloric acid, and water. Concentration of the organic layer gave yellow needles, which melted at 203-204°C after two recrystallisations from benzene or alcohol.

Yield = 0.6 gm.

Analysis

| | | | | |
|---|---|---|---|---|
| Found | | C 86.0% | H 5.5% | M.Wt. 362 |
| Required for | $C_{20}H_{14}O$ | 88.9% | 5.2% | 270 |
| | $C_{27}H_{18}O$ | 90.5% | 5.1% | 358 |
| | $C_{26}H_{18}O$ | 90.1% | 5.2% | 346 |
| | $C_{27}H_{20}O_2$ | 86.2% | 5.4% | 376 |

No dinitrophenylhydrazone could be isolated by either Allen's or Brady's method, the boiling period in the latter case being extended to 35 hours.

Oximation of "Benzylidene perinaphthanone"

A solution of the benzylidene compound (0.2 gm.) and hydroxylamine hydrochloride (1.0 gm.) in pyridine (10 ml.) was boiled under reflux for 18 hours. The orange solution was concentrated to half the original volume, cooled, poured into water (20 ml.) and extracted with ether. The yellow solution was washed with dilute hydrochloric acid (3 x 10 ml.) and with water (2 x 10 ml.). After drying over sodium sulphate for ½ hour, ether was removed. The residual brown oil on trituration with light petroleum (5 ml.) gave a

yellow solid M.Pt. 180-83°C. This crystallised from alcohol as golden needles M.Pt. 185-186°C with decomposition.

Analysis

| | | | |
|---|---|---|---|
| Found | C 82.5% | H 5.4% | N 3.1% |
| Required for $C_{20}H_{15}NO$ | 84.2% | 5.3% | 4.9% |
| $C_{27}H_{21}NO_2$ | 82.8% | 5.4% | 3.5% |

The Attempted Interaction of Ethyl Acetoacetate with "Benzylideneperinaphthanone"

A solution of redistilled ethyl-acetoacetate (0.4 gm.; $3.3 \times 10^{-3}$ mole) in absolute ethanol (15 ml.) was treated with sodium (0.2 gm.), followed by the benzylidene compound (0.45 gm.). The yellow solution was boiled under reflux for 3 hours, and poured into water. The yellow suspension was extracted with ether/ethylacetate, and the organic extract chromatographed on alumina (4" x ½"). Elution with ether removed a homogeneous yellow band, which on concentration left a reddish brown oil. Trituration of this with light petroleum gave a yellow solid, M.Pt. 79-84°C. Two recrystallisations from 60/80 light petroleum gave yellow plates (0.32 gm.), M.Pt. 89-90°C.

Analysis

| | | | |
|---|---|---|---|
| Found | C 89.0% | H 5.1% | M.Wt. 239-262 |
| Required for $C_{26}H_{22}O_3$ | 81.7% | 5.8% | 382 |
| $C_{20}H_{14}O$ | 88.9% | 5.2% | 270 |

This product was likewise obtained when the above procedure was carried out, but omitting the addition of ethyl acetoacetate. Its ultraviolet absorption spectrum resembled closely that of perinaphthenone.

The compound gave a dinitrophenylhydrazone (Brady's method) after 4 hours heating. This crystallised from tetralin or nitrobenzene as red plates, M.Pt. 229-230°C.

Analysis

| | | |
|---|---|---|
| | Found | N 11.9% |
| $C_{26}H_{19}O_4N_4$ | Requires | N 12.4% |

The Interaction of Perinaphthanone and p.-chlorobenzaldehyde

Perinaphthanone (1.0 gm.) was dissolved in 4% ethanolic KOH (15 ml.) and p.-chlorobenzaldehyde (0.95 gm.; 20% excess) added, with slight warming on the water bath to achieve solution. Rapid darkening occurred, and within 10 minutes a yellow solid commenced to separate. After standing for 45 minutes, the product was filtered off, and crystallised twice from benzene to give opaque needles, M.Pt. 231-5°C. Yield = 0.24 gm.

The melting point remained unaltered after further crystallisation from alcohol; chromatographing a portion in 1:1 benzene/ether was likewise unsuccessful in securing a sharper melting point. The material

appeared perfectly homogeneous under the microscope, and analysed as shown.

| | | | | |
|---|---|---|---|---|
| Found | | C 71.6% | H 4.9% | Cl 15.8% |
| Required for | $C_{20}H_{13}OCl$ | 78.8% | 4.3% | 11.6% |
| | $C_{27}H_{16}OCl_2$ | 75.9% | 3.8% | 16.6% |
| | $C_{27}H_{18}O_2Cl_2$ | 72.7% | 4.1% | 15.9% |

The Attempted Interaction of Ethyl Acetoacetate with "p. Chlorobenzylideneperinaphthanone"

A solution of redistilled ethylacetoacetate (0.16 gm.; $1.2 \times 10^{-2}$ mole) in absolute ethanol (15 ml.) was treated with sodium (0.2 gm.), followed by portion-wise addition of the p. chlorobenzylidene compound (0.3 gm.). The yellow solution was boiled under reflux for 3½ hours, and poured into water. The yellow suspension was extracted with benzene/ether, concentrated, and chromatographed on alumina (4" x ½"). Elution with 1:1 benzene/light petroleum removed a yellow band, which when concentrated furnished yellow plates. When crystallised from light petroleum (80-100°C) these melted sharply at 120-1°C.

Analysis

| | | | | | |
|---|---|---|---|---|---|
| | Found | C 77.8% | H 4.4% | Cl 12.0 | M.Wt. 209-230 |
| $C_{20}H_{12}OCl$ | Requires | 78.7% | 4.3% | 11.8 | 305 |

The molecular weight determination is probably inaccurate, yet it does indicate that a molecular break up has occurred. The above product was likewise

obtained when this procedure was repeated, omitting the addition of ethylacetoacetate.

The Interaction of Perinaphthanone and p.-nitrobenzaldehyde

10% Alcoholic KOH (5 ml.) was added to a solution of perinaphthanone (0.36 gm.) and p.-nitrobenzaldehyde (0.36 gm.; 20% excess) in ethanol (10 ml.). Rapid darkening occurred, and after 45 minutes the dark red precipitate was filtered off (M.Pt. 91-4°C). This solid was dissolved in benzene, and chromatographed on alumina (4" x 0.7"). With benzene as eluent, a yellow zone separated from a dark red zone, which, being retained at the top of the column, was subsequently removed by developing with ether.

Concentration of the benzene fraction provided a yellow crystalline solid (120 mgm.) which recrystallised from 2:1 benzene/light petroleum as needles, M.Pt. 167-8°C.

Analysis

| | | | | |
|---|---|---|---|---|
| Found | C 75.7% | H 4.6% | N 4.5% | M.Wt. 286 |
| Required for $C_{20}H_{13}NO_3$ | 76.2% | 4.1% | 4.4% | 315 |

Concentration of the red ether solution gave but traces of an orange solid, together with a red non-crystallisable gum. The orange solid melted at 154-168°C and, when crystallised from benzene/light petroleum, provided a further 10 mgm. of solid, M.Pt. 167-8°C.

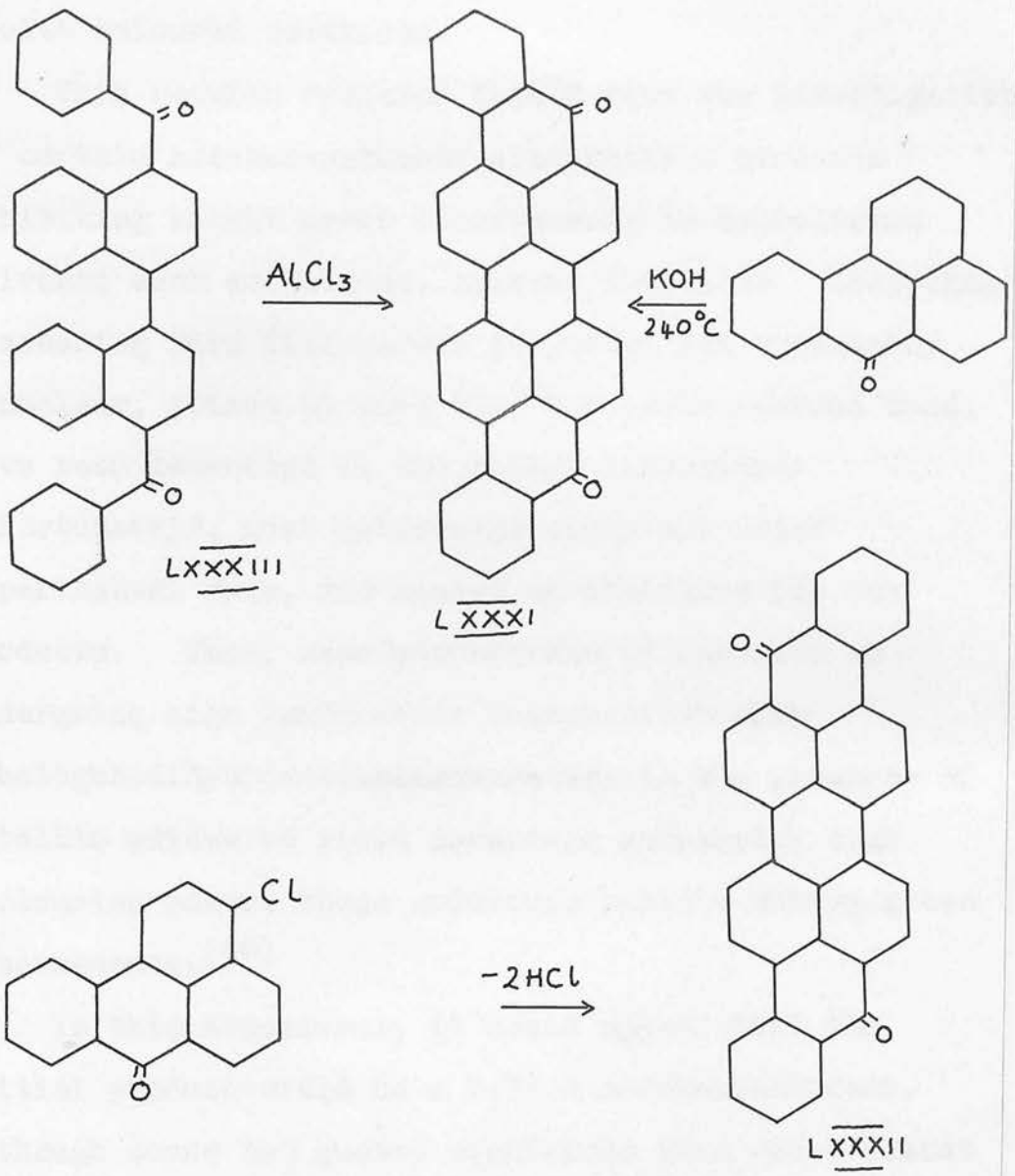
## Some Aspects of the Chemistry of Dimesobenzanthrones

### DISCUSSION

Of all the theoretically possible dimesobenzanthrones, extensive investigation of the synthesis and properties of only two such compounds has been undertaken.

Violanthrone (LXXXI) (3:3'-3:3'-dimesobenzanthrone) and the symmetrical isomeride iso-violanthrone (LXXXII) (3:4'-4:3'-dimesobenzanthrone) have merited this attention since these compounds and their derivatives are vat dyes of exceptional fastness and stability.

The former was first prepared by fusion of mesobenzanthrone with alkali[1], yet Scholl and Seer[76] performed an unequivocal synthesis by the aluminium chloride cyclodehydrogenation of 4:4'-dibenzoyl-1:1'-dinaphthyl (LXXXIII), and demonstrated the formation of (LXXXII) from the alcoholic potash fusion of 3-chloromesobenzanthrone.




The only other rigidly orientated dimesobenzanthronyls described are those in which the component mesobenzanthrone nuclei are united only by one carbon - carbon bond. 2:2'-(77), 3:3'-(78), 4:4'-(79), and 6:6'-(36) dimesobenzanthrones are reported in the literature. Such compounds are high melting, and, in

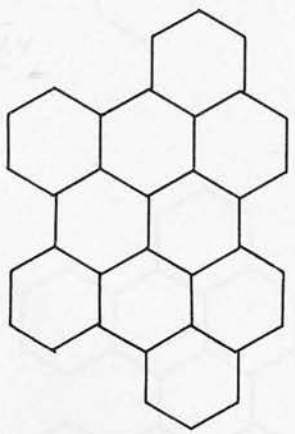
the main, dissolve in sulphuric acid to give red or violet coloured solutions.

This section concerns itself with the investigation of certain mesobenzanthrone condensation products exhibiting bright green fluorescence in hydrocarbon solvents such as benzene, xylene, tetralin. Compounds possessing this fluorescent property, and presumably binuclear, joined by more than one carbon-carbon bond, have been described in the patent literature. Unfortunately, such references carry but brief experimental data, and hazard no structure for the products. Thus, mesobenzanthrene is reported as undergoing high temperature condensation with 7-halogenodihydromesobenzanthrenes, in the presence of metallic oxides to yield materials possessing high colouring power, whose solutions exhibit strong green fluorescence.(80)

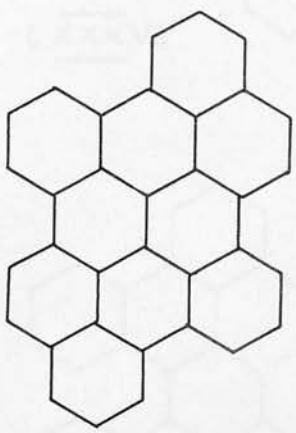
In this experiment, it would appear that the initial product would be a 7:7'-dimesobenzanthrene, although under the quoted conditions this would almost certainly dehydrogenate to the ethylenic structure (LXXXVII), and a further cyclisation of this is by no means debarred.

By passing mesobenzanthrone vapour over a heated mixture of zinc dust and pumice, Zinke et al(20) isolated as main products mesobenzanthrene and dihydromesobenzanthrene (see Introduction). Together

with these, three high melting solids were obtained in small quantity after a laborious fractionating process. The first solid crystallised from quinoline in dark red plates, M.Pt. 416-8°C, and was identified as a mixture of violanthrene and isoviolanthrene on the basis of its giving a blue colour with sulphuric acid, and undergoing mild oxidation to the ketones (LXXXI) and (LXXXII). Solid 2 (crystallised from xylene) was golden yellow, melting point 407-8°C, and in sulphuric acid gave a red-yellow colour, which subsequently turned to violet-brown. Its xylene solution had a pale green fluorescence, and the compound, analysing for $C_{34}H_{16}$, was formulated as either the cis (LXXXIV) or trans (LXXXIVa) isomer of dibenzomesonaphthodianthrene.

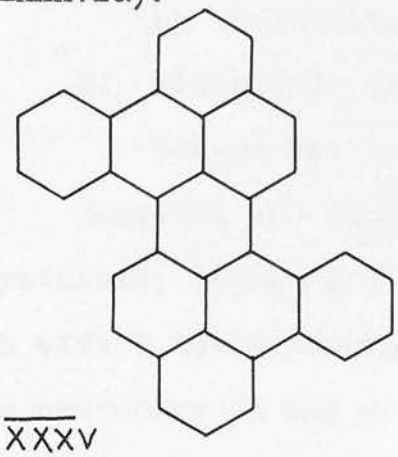


LXXXIV

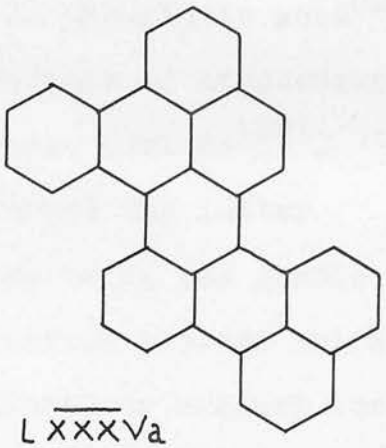


LXXXIVa

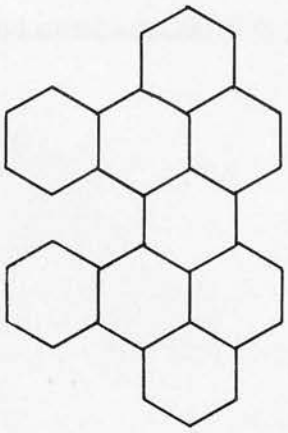
The third component (melting point 341-2°C), a yellow crystalline solid, whose solutions exhibited strong green fluorescence, dissolved in sulphuric acid to give a violet solution, and analysed for $C_{34}H_{18}$. Since this compound was recovered unchanged after heating it with aluminium chloride, it was inferred that the two mesobenzanthrone nuclei were so united as to preclude further cyclisation being possible. Accordingly, this substance was regarded as having structure (LXXXV) or (LXXXVa) rather than (LXXXVI) or (LXXXVIa).



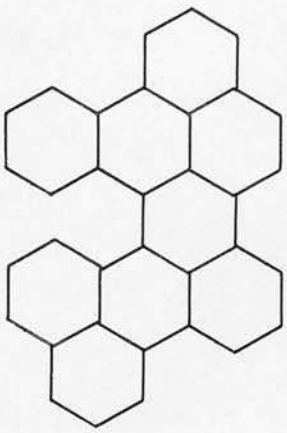
L$\overline{\text{XXX}}$V



L$\overline{\text{XXX}}$Va



L$\overline{\text{XXX}}$VI



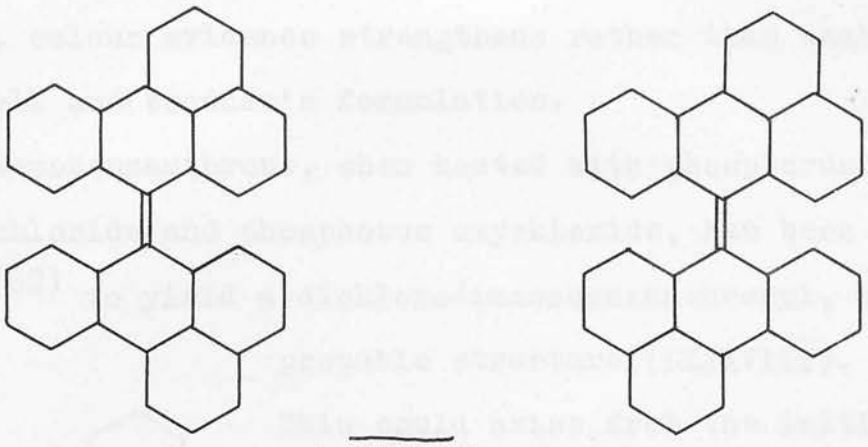
L$\overline{\text{XXX}}$VIa

One would expect the mesonaphthodianthrones (LXXXIV) and (LXXXIVa) to be similarly unaffected by aluminium chloride. Zinke's argument thus appears to rest entirely on the not unreasonable assumption that the higher melting compound (407-8°C) would be the more condensed ring system.

The material, M.Pt. 341-2°C, has also been synthesised by two other methods.

1. Mesobenzanthrone and mesobenzanthrene are condensed at high temperature in the presence of condensing agents such as phosphoric acid[81].
2. Phosphorus oxychloride solutions of mesobenzanthrone are boiled for extended periods[22].

Campbell and Woodham, who performed the latter synthesis, regarded such treatment as being too gentle to effect the dehydrogenation/dehydration process which is necessary in any mechanism postulated to account for the formation of the yellow compound. These workers suggested the existence of an ethylenic structure, i.e. 7:7'-dimesobenzanthrylidene (LXXXVII).



LXXXVII

Such a compound contains two hydrogen atoms less than Zinke's proposed structure, but the differences in the percentage composition of all such molecules is so small that analysis cannot provide an unambiguous method of differentiation.

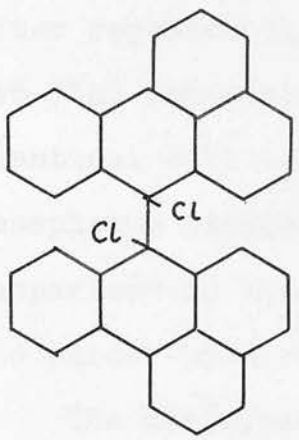
| | | | |
|---|---|---|---|
| Required for | $C_{34}H_{20}$ | C 95.3% | H 4.7% |
| | $C_{34}H_{18}$ | 95.7% | 4.3% |
| | $C_{34}H_{16}$ | 96.2% | 3.8% |

The serious drawback to an ethylenic structure is that it would hardly be unaffected (i.e. remain uncyclised) when heated with aluminium chloride.

The suggestion has been made[37] that, by analogy with 9:9'-difluorenylidene and 9:9'-dixanthylidene, a compound with the proposed ethylenic structure should be red, or bluish-green. A better comparison would have been with the more closely related 9:9'-dianthrone

which, like (LXXXVII), possesses an extended para-quinonoid system, and is bright yellow. On this basis, colour evidence strengthens rather than weakens Campbell and Woodham's formulation.

Mesobenzanthrone, when heated with phosphorus pentachloride and phosphorus oxychloride, has been shown[82] to yield a dichlorodimesobenzanthrenyl, of probable structure (LXXXVIII). This could arise from the initial formation and subsequent chlorination of 7:7'-dimesobenzanthrylidene.




LXXXVIII

Neither the British nor the Continental workers have recorded attempts at identification by degradative methods, and it was felt that such an approach might throw some light on the problem. The recovery of starting material from oxidations with hydrogen peroxide and potassium permanganate[37] showed that these reagents were too mild to degrade the molecule.

Chromium trioxide, so often successful for mesobenzanthrones, would be expected to rupture (LXXXVII) with formation of anthraquinone-1-carboxylic acid. On the other hand, if the structure of the condensation product was that of a tetrabenzperylene, the degradation products would, in all probability, be

comprised of a difficultly separable mixture of poly-carboxylic acids and quinones.

Thus, whilst no rigid conclusions may be drawn for the peropyrene derivatives, structure (LXXXVII) is largely proved or disproved by the isolation of (or failure to isolate) anthraquinone-1-acid from chromium trioxide treatment of the condensation product.

Repetition of the $PCl_5/POCl_3$ experiment gave, after repeated chromatography, a yellow compound (M.Pt. 346-7°C) containing no chlorine. This was shown identical with the substance obtained on heating a phosphorus oxychloride solution of mesobenzanthrone by comparison of the ultraviolet absorption spectra and by the colour produced with $H_2SO_4$.

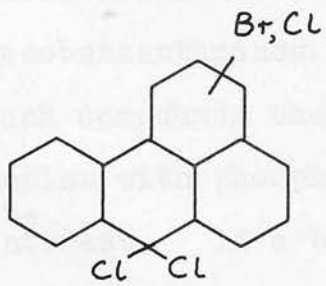
The attempted oxidation of this substance with chromium trioxide resulted in a quantitative recovery of starting material; on this basis, it is doubtful if the condensation product is a dimesobenzanthrylidene.

In an attempt to synthesise (LXXXVII) R.A. Wall[37] had recourse to the preparation of 7:7'-dichloromeso-benzanthrene by the $PCl_5$ fusion of mesobenzanthrone. Instead of the desired product, an impure substance was obtained which analysed for a trichloromesobenzanthrene. Obviously some attack on the aromatic nucleus must have occurred, probably in the 3-position.

This reaction was therefore repeated in an attempt to orientate the compound by oxidation. Chromatographic

methods proved unsuccessful in effecting any separation beyond a preliminary removal of tars, and the best method of purification was the reprecipitation of the substance from a benzene solution by light petroleum. In this manner, a dark red material was isolated which melted some twenty degrees higher than reported, and an analysis indicated that it was a mixture of tri- and tetra-chloromesobenzanthrenes. Further purification could not be effected, and once again an unexpected resistance to oxidation was encountered.

During this research, a reference to the action of phosphorus pentachloride on a solution of 1- (or 2-) nitro-3-bromomesobenzanthrone in nitrobenzene was noted(83). In the course of this reaction the nitro group is somewhat surprisingly eliminated, and the colourless product (LXXXIX) is suggested as being the bromochloro-7,7'-dichloromesobenzanthrene. It is unfortunate that since this paper was only available to us in the abstracted form, no experimental details were available. It might be expected that the only function of the nitrobenzene would be that of a diluent; were this so, the product from the phosphorus pentachloride fusion of mesobenzanthrone should be identical with that obtained in the presence of nitrobenzene, and that the chloro-




LXXXIX

7,7'-dichloromesobenzanthrene might be an intermediate for the synthesis of (LXXXVII). However on heating the unsubstituted ketone with $PCl_5$ and nitrobenzene, two impure chlorinated amorphous red solids of widely differing melting point were isolated in poor yield, accompanied by tars and carbonaceous matter.

Both solids were resistant to oxidation, and the higher melting material possessed vatting properties resembling the violanthrones. Neither substance could be obtained in a sufficient degree of purity to warrant an analysis, and further work on them was abandoned.

The presence of suitably placed groups in the mesobenzanthrone molecule should function as an effective means of blocking a specific position, thereby preventing such a position from taking part in a bimolecular link.

The first section of this Thesis has indicated the difficulties attendant in the synthesis of 8-substituted mesobenzanthrones. Should a preparation be found for such compounds the results obtained from their interaction with phosphorous halides would be of great interest. If a bimolecular condensation took place, it is patent that the 8-position could not form part of the cyclic structure, and hence such structures as (LXXXIV), (LXXXVa) and (LXXXVIa) would be eliminated from consideration.

The interaction of 8-substituted mesobenzanthrones

with Grignard reagents would give access to 6,8-disubstituted products; the ethylenic structure (LXXXVII) would be favoured should these condense in the presence of $PCl_5/POCl_3$.

Again, the greater reactivity of the 6-position (naphthalene half) as opposed to the 8-position (phenyl half)[36] would point to a 6:6' link being preferable to 6:8' or 8:8' bonding, and thus discredit structures (LXXXVa) and (LXXXVIa).

Examination of the condensation of 6-substituted mesobenzanthrones is by similar reasoning of pertinence.

The present research demonstrates the absence of any fluorescing solutions and generally good recovery of starting material when the 6-chloro and 6-phenyl compounds were treated with $POCl_3$ and $POCl_3/PCl_5$.

Further, 6:6'-dimesobenzanthronyl gave strongly green fluorescing solutions, from which only traces of a non-characterisable high melting solid was obtained.

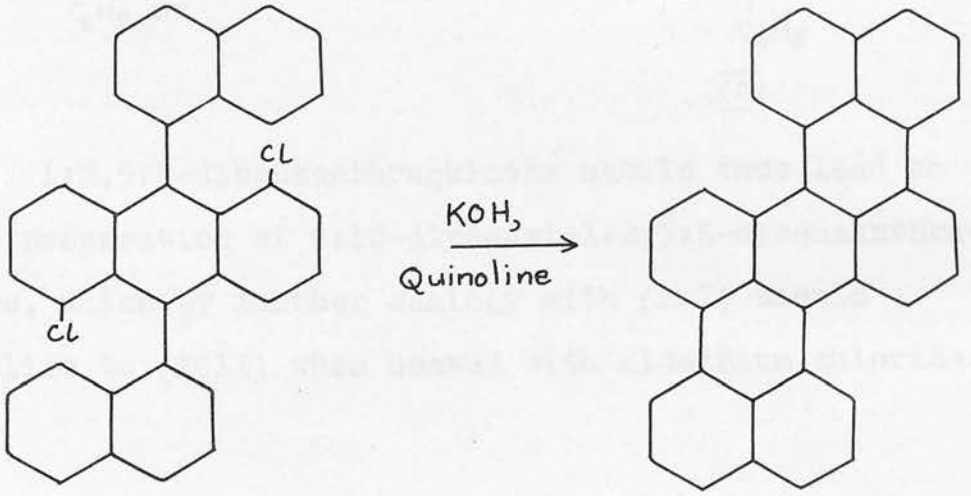
Under similar reaction conditions, anthraquinone remained totally unaffected.

The foregoing evidence, then, favours the condensation product (M.Pt. 341-2°C) being formulated as (LXXXIV), (LXXXV), or (LXXXVI).

However such reasoning is based largely on negative results, and a natural corollary was the synthesis of some of the theoretically possible bimolecular structures in order to compare their

physical properties (e.g. colour, ultraviolet absorption spectra, melting point) with those of the $POCl_3/PCl_5$ products.

One such compound, the blue 7:8'- 8:7'-dimesobenzanthrone, (XC), M.Pt. 333-4°C, has been prepared in unspecified yield by ring closure of 1:5-dichloro-9:10-di-1-naphthylanthracene.(84)




XC

The present work records unsuccessful attempts to isolate four related hydrocarbons, viz:

a. 6:7'- 7:6'-Dimesobenzanthrone (XCII)

b. 7:7'- 8:8'-Dimesobenzanthrone (XCIII)

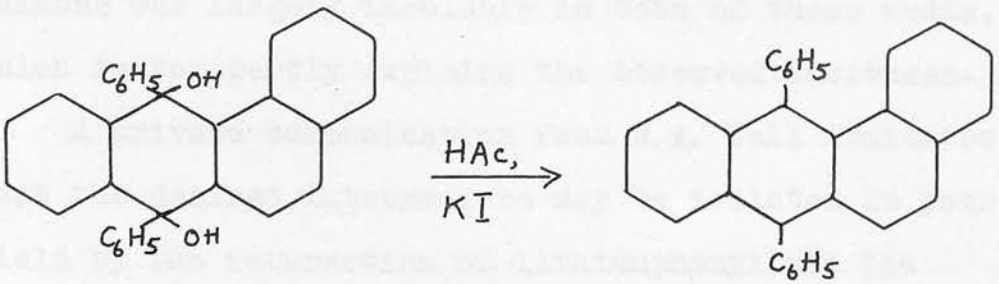
c. 7:7'-Dimesobenzanthrylidene (LXXXVII)

d. 6:6'- 7:7'- 8:8'-Dimesobenzanthrone (LXXXIV)

a. 6:7'- 7:6'-Dimesobenzanthrone (XCII)

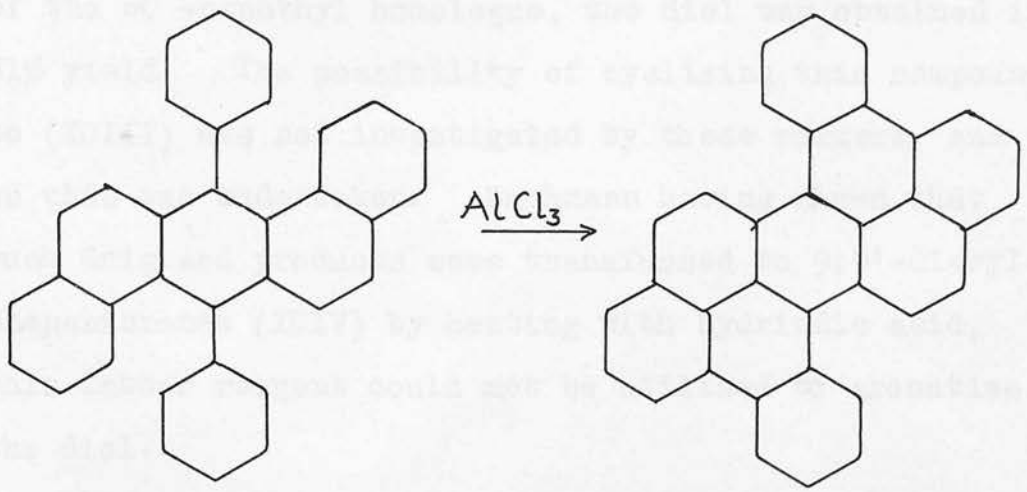
The preparation of 9:10-diphenyl-1:2-benzanthracene (XCI) has been achieved by reduction of the

diol obtained from the interaction of 1:2-benzanthra-9:10-quinone with phenylmagnesiumbromide.(85)




XCI

1:2,5:6-dibenzanthraquinone should thus lead to the preparation of 9:10-diphenyl-1:2,5:6-dibenzanthracene, which by further analogy with (XCI) should cyclise to (XCII) when heated with aluminium chloride.



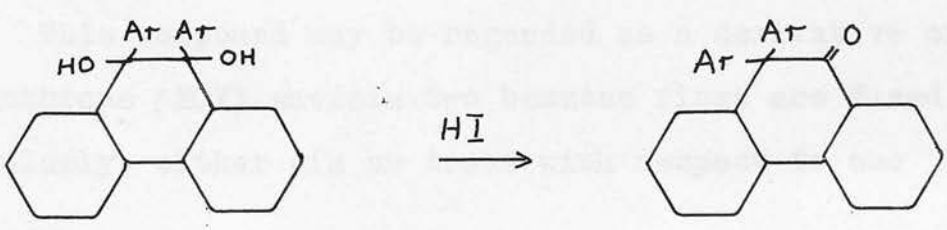

XCII

Unfortunately these surmises could not be tested on account of the lack of interaction of the quinone and the Grignard reagent. The reaction was performed in boiling di-isoamylether and diphenylether; the quinone was largely insoluble in both of these media, which factor partly explains the observed inertness.

A private communication from R.A. Wall indicates that the desired intermediate may be isolated in poor yield by the interaction of lithiumphenyl and the quinone, but the small scale $AlCl_3$ cyclisation of this provided no identifiable product.

b. 7:7'- 8:8'-Dimesobenzanthrone (XCIII)

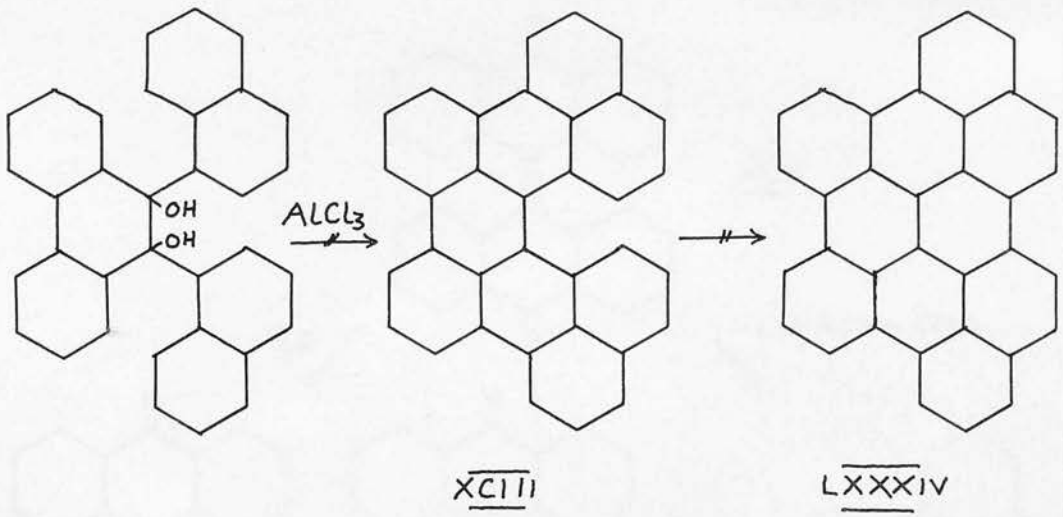
Bachmann and Ju-Hwa-Chu[86] have prepared a series of 9:10-diarylphenanthrene-9:10-diols by reacting phenanthraquinone with Grignard reagents. In the case of the $\alpha$ -naphthyl homologue, the diol was obtained in 31% yield. The possibility of cyclising this compound to (XCIII) was not investigated by these workers, and so this was undertaken. Bachmann having shown that such Grignard products were transformed to 9:9'-diaryl-phenanthrones (XCIV) by heating with hydriodic acid, this latter reagent could not be utilised to aromatise the diol.




XCIV

An alternative method of effecting reduction with zinc dust and acetic acid proved unsuccessful. The $AlCl_3$ cyclisation of the diol was therefore attempted. From this reaction a small quantity of an impure white solid, partly melting at 158-59°C, the remainder at 290-300°C, was isolated. This differed from starting material (M.Pt. 262-3°C) but could not be purified sufficiently to justify an analysis.

The probability of this substance being either of the cyclised structures (XCIII) or (LXXXIV) is therefore excluded, on account of absence of colour and the low melting point.



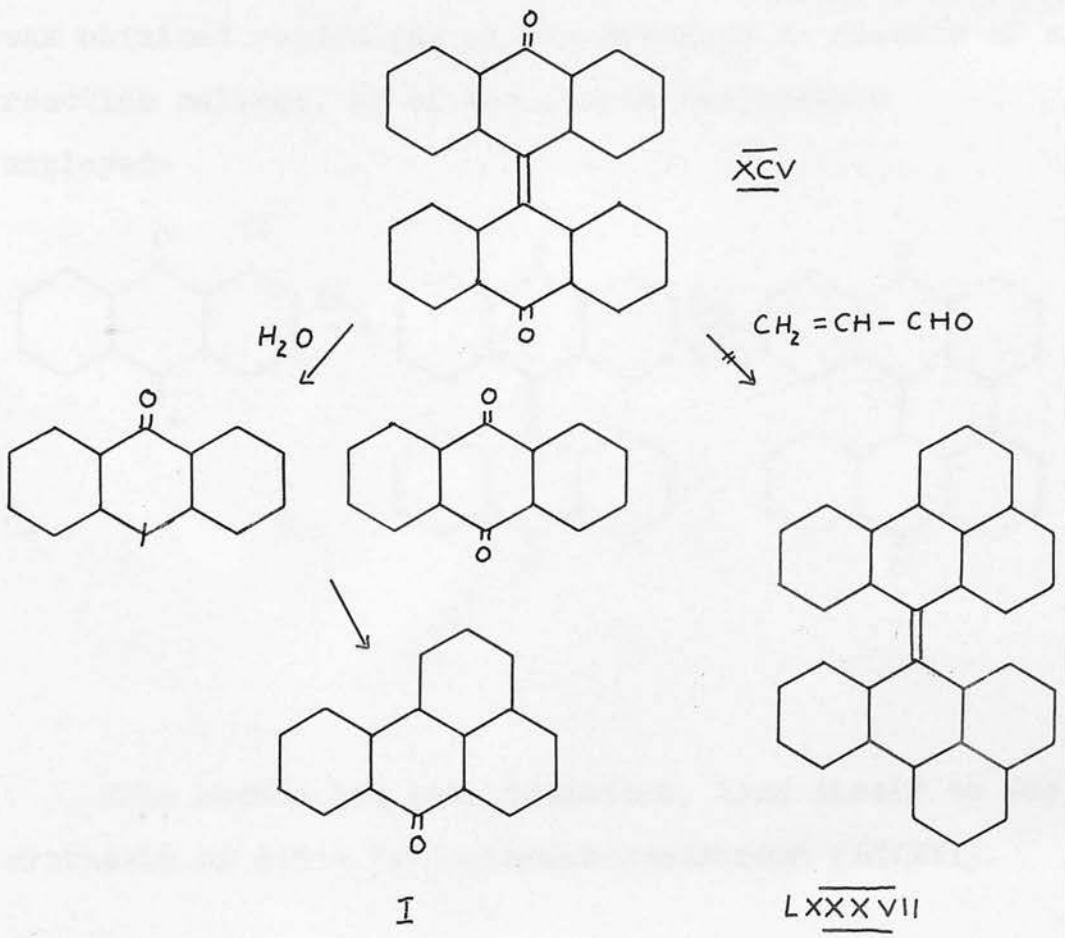

XCIII LXXXIV

c. 7:7'-Dimesobenzanthrylidene (LXXXVII)

This compound may be regarded as a derivative of dianthrone (XCV) wherein two benzene rings are fused angularly, either cis or trans with respect to one

another.

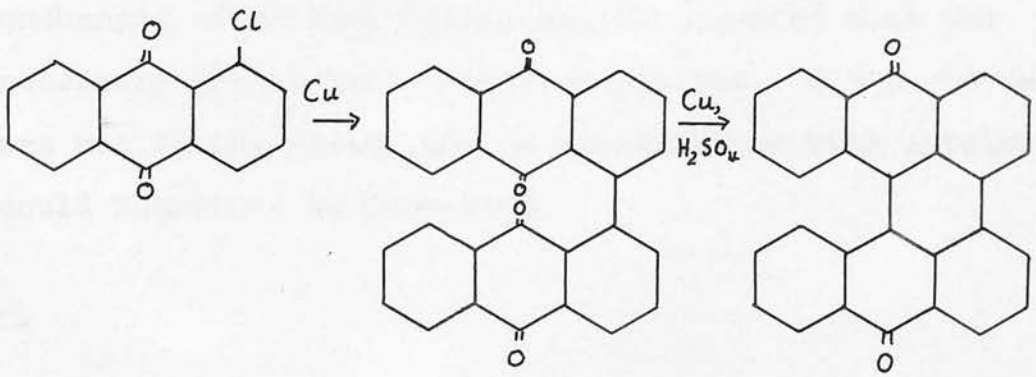
Viewed in such a light, a logical means for the preparation of this substance would be the condensation of (XCV) with two molecules of acrolein. When this reaction was performed, only mesobenzanthrone was isolated. A blank test, where glycerol was omitted, demonstrated that dianthrone readily underwent hydrolytic cleavage to yield anthraquinone and anthrone, a fact noted elsewhere.(87) In the present reaction, it is clear that the acrolein has combined with the anthrone generated in situ, with formation of the parent ketone.



d. 6:6'- 7:7'- 8:8'-Dimesobenzanthrone (LXXXIV)

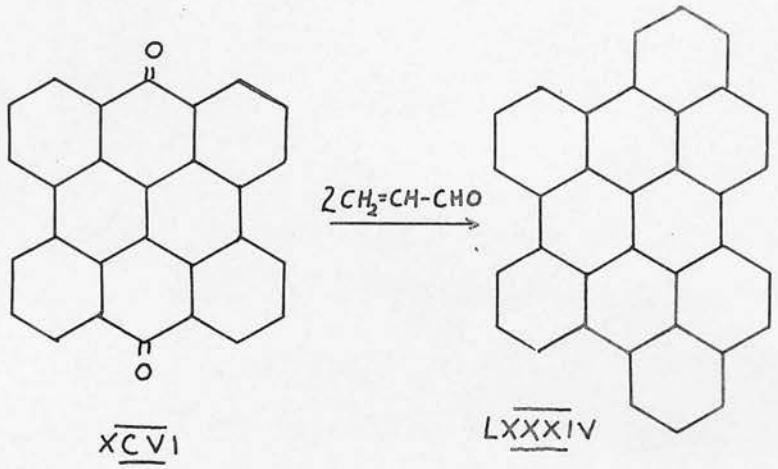
The previously observed facile cleavage of dianthrone preventing the synthesis of (LXXXVII) by Bally's method, it was hoped that further bonding in the dianthrone molecule would provide a structure wherein the ethylenic (C 7) bond would exhibit greater stability.

Attempts to synthesise helianthrone by the method of Scholl and Mansfeld[88] were singularly unpromising. In a series of fusions of 1-chloroanthraquinone with copper bronze, a brick red amorphous substance was repeatedly isolated, whose diffuse melting point indicated a low degree of purity. The same material was obtained regardless of the presence or absence of a reaction solvent, or of the fusion temperature employed.




This method did not, therefore, lend itself to the synthesis of 6:6'- 7:7'-Dimesobenzanthrone (LXXXVI).

The formation of the high melting mesonaphthodianthrone (XCVI) from exposure of dianthrone to ultraviolet light[89] indicated a possible synthesis for (LXXXIV) by interaction of (XCVI) with acrolein.




XCVI LXXXIV

Since mesonaphthodianthrone was recovered unchanged after such reactions, it appeared that the necessary preliminary reduction process $C = O \longrightarrow CH_2$ was not taking place, and no condensation with acrolein could therefore be permitted.

## EXPERIMENTAL

### Some Aspects of the Chemistry of Dimesobenzanthrones

### The Interaction of Mesobenzanthrone with phosphorus oxychloride and phosphorus pentachloride

Phosphorus pentachloride (8.0 gm.) was added to the dark red solution obtained by dissolving mesobenzanthrone (5.0 gm.) in phosphorus oxychloride (100 ml.). When the mixture was boiled under reflux for 5 hours, the colour changed to dark brown, and a black rim was deposited on the side of the flask. Excess phosphorus oxychloride was distilled off, the black residue was allowed to cool, and water (25 ml.) added cautiously. The resulting black suspension was filtered, and the solid extracted for 35 hours with benzene or xylene in a Soxhlet apparatus. The green fluorescing solution was concentrated to 75 ml., filtered from a carbonaceous residue (0.5 gm.) and chromatographed on alumina (25 cm. x 4 cm.). With benzene as eluent, a bright yellow zone was rapidly eluted, to give a vivid green fluorescing solution (A). Further development of the column with benzene slowly washed off a dark brown zone, which, on evaporation, provided an intractable black tar (3.4 gm.).

Solution (A) was concentrated to 25 ml., and filtered hot, thereby separating a bright yellow precipitate (35 mgm.).

Thorough cooling of the filtrate provided a further

10 mgm. of the compound, which crystallised from boiling xylene as yellow micro needles, M.Pt. 346-47°C. Treatment of a sample of this with concentrated sulphuric acid gave a green colour, turning rapidly to violet.

The spectrum of the substance (in chloroform) showed a distinct resemblance to the spectrum of tetrabenzperylene, and was shown identical with the material isolated by Campbell and Woodham[22], M.Pt. 341-2°C.

Attempted oxidation of the compound - M.Pt. 346-7°C.

Chromium trioxide (100 mg.) was added to a suspension of the above compound (40 mg.) in boiling acetic acid (10 ml.). After 5 hours, the solution was cooled, and poured into cold water (100 ml.). Unchanged starting material (M.Pt. and Mixed M.Pt.) was recovered quantitatively.

The Interaction of 6-Phenyl-mesobenzanthrone with phosphorus oxychloride and phosphorus pentachloride

6-phenyl-mesobenzanthrone (3.0 gm., prepared by the method of Allen and Overbaugh, J.A.C.S. 1935, 57; 740) was added to phosphorus pentachloride (3.5 gm.) in phosphorus oxychloride (40 ml.). The mixture was boiled under reflux, and after 1 hour's heating the initial crimson red colour had changed to dark green. After heating for a period of 8 hours, excess phosphorus

oxychloride was distilled off, the black solid allowed to cool, and any residual phosphorus pentachloride decomposed by cautious addition of water (25 ml.).

A brown non-fluorescing solution was obtained on Soxhlet extraction of the dried black residue (4.5 gm.) with benzene or xylene. This solution was concentrated to 50 ml., and chromatographed on alumina (9" x 1"). A broad yellow zone washed through, when 1:1 benzene/ether was used as eluent.

Evaporation of this solution gave a yellow solid (2.7 gm.), crystallising from acetic acid or from chlorobenzene to form yellow needles (2.54 gm.), M.Pt. 185-186°C. This melting point remained undepressed when admixed with 6-phenyl-mesobenzanthrone. (Recovery = 83%)

No further crystalline material could be obtained from the column.

6-amino-mesobenzanthrone

Mesobenzanthrone (30 gm.) was aminated as directed by Bradley (J.C.S. 1948, 1175). It was found that during the final liberation of the free amine, vigorous stirring was essential. If this stirring was omitted, a dark red gum invariably formed.

The product was recrystallised twice from ethanol, and was obtained as yellow needles, M.Pt. 185-186°C. (lit 186°C.).

Yield 17.5 gm. (62%).

6-chloro-mesobenzanthrone

6-amino-mesobenzanthrone (12.0 gm.) was diazotised by Hodgson's method, and the diazonium sulphate converted to 6-chloro-mesobenzanthrone, as directed by Bradley and Jadhav (J.C.S. 1948, 1624).

The product crystallised from alcohol to yield yellow needles, M.Pt. 145-146°C. (lit 146-7°C.).

Yield = 9.3 gm. (72% theoretical).

6-6' Dimesobenzanthronyl - (cf. Bradley and Jadhav, ibid)

The product was obtained as yellow needles, which, after two recrystallisations from nitrobenzene, melted at 358-59°C.

Yield (from 4 gm. chloro-compound) = 0.8 gm. (23%).

The Reaction of 6-chloro-mesobenzanthrone with phosphorus oxychloride and phosphorus pentachloride

6-chloro-mesobenzanthrone (2.4 gm.) was dissolved in phosphorus oxychloride (25 ml.) and phosphorus pentachloride (2.4 gm.) added to the crimson solution. The mixture was boiled under reflux for 5 hours, and considerable darkening occurred. Excess phosphorus oxychloride was distilled off, and the black residue triturated with cold water (15 ml.). Continuous extraction of the dried solid with benzene (250 ml.) resulted in an orange red solution, exhibiting no marked fluorescence. This solution was concentrated to 75 ml., and chromatographed on alumina (8½" x 1½");

with benzene as eluent, a yellow zone was separated from a dark brown layer retained at the top of the column. The yellow zone, on concentration, deposited yellow needles (1.8 gm.). After one crystallisation from alcohol, these melted at 143-145°C, and, by mixed melting point, were established as crystals of 6-chloro-mesobenzanthrone. A further 0.25 gm. was obtained from the mother liquor. Recovery = 86%.

The Reaction of Anthraquinone with phosphorus oxychloride and phosphorus pentachloride

A mixture of anthraquinone (5.0 gm.), phosphorus pentachloride (5.5 gm.) and phosphorus oxychloride (100 ml.) was heated for 15 hours. At no stage did solution occur, and a quantitative recovery of anthraquinone was effected by working up in the usual manner.

The Reaction of 6-6'-Dimesobenzanthronyl with phosphorus oxychloride and phosphorus pentachloride

6-6'-Dimesobenzanthronyl (0.5 gm.) was dissolved in phosphorus oxychloride (25 ml.) and phosphorus pentachloride (0.9 gm.) added to the resultant deep red solution. The mixture was heated under reflux for 5 hours, cooled, concentrated, and decomposed in the usual manner.

A solution with strong green fluorescence was obtained by continuous extraction of the shining black

residue (0.63 gm.) with benzene. This solution was concentrated, filtered, and columned on alumina (1" x 5"). Elution with benzene removed a yellow band, possessing green fluorescence. Traces of a light yellow solid (< 5 mgm.), M.Pt. > 360°C was obtained by removal of solvent. This solid was insoluble in concentrated sulphuric acid.

Development of the column with ethyl acetate removed a brown zone, possessing pale green fluorescence in ultraviolet light. This fraction furnished a minute quantity of a yellow solid, M.Pt. 358°C, with sublimation at 310°C. This solid dissolved in benzene to give a strong green fluorescent solution.

The Interaction of Phosphorus pentachloride and mesobenzanthrone in nitrobenzene

Phosphorus pentachloride (3.5 gm.) was added to a suspension of mesobenzanthrone (2.5 gm.) in nitrobenzene (150 ml.). The mixture was heated under reflux on an oil bath for 8 hours, after which time water (20 ml.) was added, the mixture was well shaken, and nitrobenzene removed by steam distillation.

The black solid was filtered, dried, and extracted with benzene to yield the familiar dark green fluorescing solution. This was concentrated to 50 ml., filtered from a precipitated carbonaceous residue, and chromatographed on alumina (12" x 1¾").

On elution with benzene, first an orange band, and second a dark red band separated from a dark region at the column head. Both fractions, on separate elution, possessed green fluorescence.

The orange fraction was concentrated to 25 ml. Addition of 60-80° light petroleum (25 ml.) precipitated a red solid [A], found to contain halogen. This solid, m.p. > 400°C, darkened and sintered at 278-280°C.

The dark red fraction was concentrated, and a carmine red solid [B] was precipitated by addition of an equal volume of light petroleum. This solid melted over a range 197-203°C, which was raised to 204-206°C after repeated washing with warm petrol ether (80/100°C). Further purification of either [A] or [B] was unable to be effected.

The Attempted Oxidation of Solid [A]

The solid (0.02 gm.) was suspended in boiling acetic acid (10 ml.) and chromium trioxide (0.08 gm.) added. After 3 hours, the mixture was cooled and unchanged starting material (identified by sintering point) recovered quantitatively.

The Attempted Oxidation of Solid [B]

The carmine granules (15 mgm.) were boiled with acetic acid (5 ml.) and chromium trioxide (20 mgm.) for periods up to 30 hours. Invariably, quantitative recovery of starting material (as identified by mixed M.Pts.) was effected.

The Fusion of Mesobenzanthrone with phosphorus pentachloride - cf. R.A. Wall, Thesis, Edinburgh University

A 250 ml. flask, containing an intimate mixture of mesobenzanthrone (5 gm., 0.022 mole.) and phosphorus pentachloride (10 gm., 0.047 mole.) was heated for two hours on an oil bath, maintained at 175-180°C. Decomposition with ice water (30 gm.) yielded a dark brown solid (6.5 gm.) which was continuously extracted with benzene. The resulting dark red solution was concentrated to 60 ml., and a black residue (3.1 gm.) removed by filtration. The filtrate was adsorbed on a column of alumina (10" x 1½"), which was subsequently developed with benzene. Only one zone, vivid carmine in colour, washed through.

This was concentrated to 50 ml., and an amorphous crimson solid (0.6 gm.) was precipitated by adding 60-80° petrol ether (50 ml.).

Repetition of this precipitation process, which was found to be the most effective means of purification, yielded 0.5 gm. of material, melting at 229-231°C, and containing halogen.

The solid dissolved slowly in cold sulphuric acid to give a green-blue colour. Dilution of this solution provided starting material.

A sample was rechromatographed in benzene for analysis.

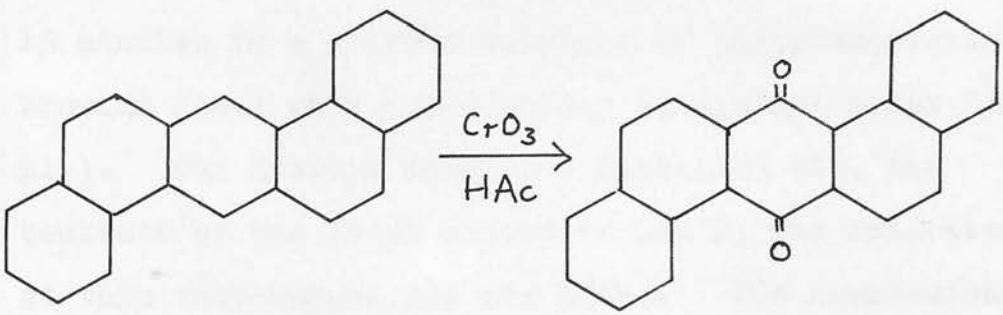
Analysis

| | | | | |
|---|---|---|---|---|
| Found | C 59.5% | H 1.9% | Cl 36.8% |
| Required for $C_{17}H_9Cl_3$ | 63.9% | 2.8% | 33.3% |
| $C_{17}H_8Cl_4$ | 57.7% | 2.3% | 40.0% |
| $C_{34}H_{15}Cl_7$ | 61.0% | 2.2% | 37.0% |

An attempt to oxidise the compound (0.25 gm.) by boiling for 2 hours with acetic acid (15 ml.) and chromium trioxide (0.35 gm.) was unsuccessful, starting material being quantitatively recovered.

The attempted preparation of 6:7',7:6'-Dimesobenzanthrone.

1:2,5:6 Dibenzanthraquinone - (cf. Clar Ber 1929, 62; 350)



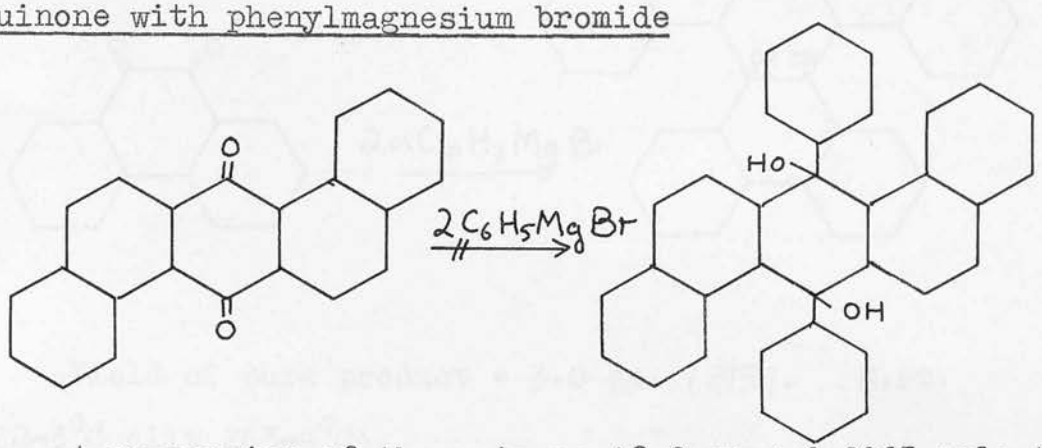

Powdered 1:2,5:6-dibenzanthracene (5 gm.) was suspended in boiling acetic acid (120 ml.) and chromium trioxide (6.0 gm.) added in 2 gm. portions over the space of 5 minutes, allowing the effervescence to subside after each addition. The quinone commenced to precipitate within 10 minutes, and after a further two hours heating, the suspension was cooled, and the dark red precipitate filtered off.

After three recrystallisations from acetic acid,

the product was obtained as orange needles, M.Pt. 239-240°C (lit. 244-245°C).

Yield 4.6 gm. (83%).

The attempted interaction of 1:2,5:6 Dibenzanthraquinone with phenylmagnesium bromide



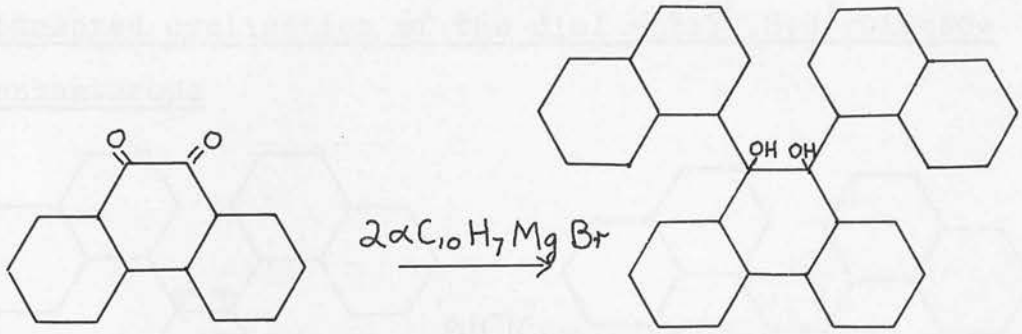

A suspension of the quinone (2.0 gm.; 0.0065 mole.) in di-isoamyl ether (150 ml.) was added over a period of 15 minutes to a stirred solution of phenylmagnesium bromide (14.1 gm.; 0.078 mole.) in diethyl ether (200 ml.). The diethyl ether was distilled off, the contents of the flask heated to 100°C, and maintained at this temperature for six hours. The suspension was poured onto a mixture of cracked ice (150 gm.) and acetic acid (15 ml.). The resulting green solid was filtered, washed with aqueous alcohol, and crystallised from acetic acid as orange needles (1.84 gm.), M.Pt. 242-245°C, undepressed on admixture with the quinone.

A similar recovery of starting material was effected when the reaction was repeated with the heating maintained at 120°C for 12 hours.

The Attempted Preparation of 7:7$^1$,8:8$^1$-Dimesobenzanthrone

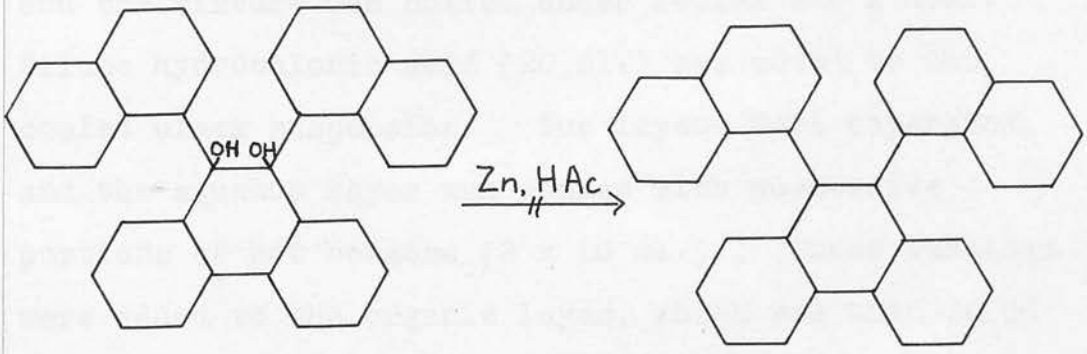
9:10-Di-α-naphthyl 9:10-dihydrophenanthrene-9:10-diol -

(cf. Bachmann and Ju-Hwa-Chu, J.A.C.S. 1935, 57; 1095-8)




Yield of pure product = 3.0 gm. (27%). M.Pt. 262-3°C (lit 263-4°C).

Attempted reduction of the diol

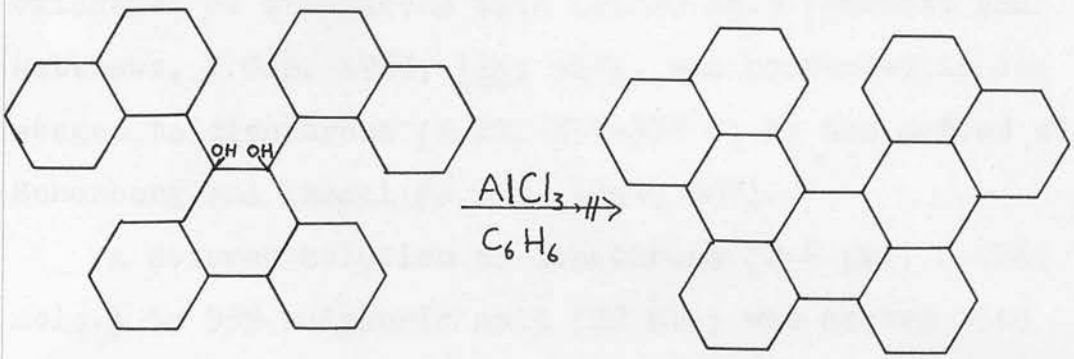



A solution of the above compound (0.5 gm.) in acetic acid (50 ml.) was treated with zinc dust (1.0 gm.) and the suspension was boiled under reflux for 2½ hours. After filtration, the solution was concentrated to 20 ml. and poured into cold water (25 ml.). The white precipitated solid was filtered, dried, and crystallised

from alcohol as prisms, M.Pt. 260-262°C, Mixed M.Pt. 259-260°C.

Recovery = 0.35 gm. (70%).

Attempted cyclisation of the diol - 7:7',8:8'-Dimeso-benzanthrone




Anhydrous aluminium chloride (3.0 gm.) was added to a solution of the diol (0.75 gm.) in dry benzene (75 ml.), and the mixture was boiled under reflux for 1 hour. Dilute hydrochloric acid (20 ml.) was added to the cooled black suspension. The layers were separated, and the aqueous layer was washed with successive portions of hot benzene (2 x 10 ml.). These washings were added to the organic layer, which was then dried overnight with anhydrous calcium chloride. Concentration of the benzene solution precipitated an "off-white" solid, M.Pt. 130-140°C. Crystallisation from light petroleum (80/100°) raised the melting point to 157-9°C. A quantity of unmelted colourless material (M.Pt. ca 300°C) was also present. This impurity was not removed by further crystallisation (charcoal screening).

The solid was dissolved in benzene and chromatographed on alumina, but only small amounts of non-crystallising oils resulted on elution of the column.

The Attempted Synthesis of 7:7'-Dimesobenzanthrylidene

Dihydrodianthrone, prepared in 68% yield by the oxidation of anthracene with nitric acid (Barnett and Matthews, J.C.S. 1923, 123; 387), was converted in two stages to dianthrone (M.Pt. 337-338°C) by the method of Schonberg and Ismail (J.C.S. 1944, 307).

A stirred solution of dianthrone (2.6 gm.; 0.0068 mole.) in 95% sulphuric acid (22 ml.) was heated with precipitated copper (1.93 gm.; 0.003 mole), the temperature being maintained at 35-45°C during this addition, and for a subsequent 45 minutes.

A mixture of glycerol (3.84 gm.; 0.042 mole.) and water (1.8 ml.) was added dropwise, the temperature allowed to rise to 90°C, and thereafter maintained at 110-112°C for 2 hours, by means of a heated oil bath.

The cooled, dark red solution was poured into boiling water (400 ml.), and the green solid so obtained was filtered, washed with hot water, and continuously extracted with xylene (250 ml.). On concentration, the liquor deposited yellow needles (0.94 gm.); M.Pt. 169-170°C, undepressed on admixture with mesobenzanthrone.

The Interaction of Glycerol and Mesonaphthodianthrone

Mesonaphthodianthrone - cf. Meyer and Bondy, Monatshefte 1912, 33; 1447.

A solution of dianthrone (3.0 gm.) in boiling acetic acid (1500 ml.) was exposed to an ultraviolet beam from a 250 watt Hanovia arc lamp for a period of 2 hours. On hot filtration, 1.9 gm. of mesonaphthodianthrone were obtained, M.Pt. > 420°C (lit > 550°C).

A further 0.8 gm. precipitated from the cooled filtrate, giving an overall 90% yield. A sample dissolved in concentrated sulphuric acid to give a deep red, orange fluorescing solution.

A stirred solution of mesonaphthodianthrone (1.5 gm.; 0.004 mole.) in 95% sulphuric acid (8.5 ml.) was treated with copper bronze (0.75 gm.; 0.0012 mole.) at 35-45°C. Glycerol (2.0 gm.; 0.02 mole.) and water (2 ml.) were added as above. The temperature was allowed to rise to 90°C, and raised to 115-118°C over a period of 75 minutes. This temperature was maintained for a further 2½ hours, when the red sludge was cooled to 50-60°C and triturated with boiling water (70 ml.). The black precipitate was extracted with nitrobenzene, xylene, and acetylene tetrachloride, and the combined extracts (250 ml.) steam distilled.

The residual dark brown flakes were filtered off, and washed with hot 80-100° petrol ether, to give yellow plates, somewhat impure, M.Pt. > 420°C. These

plates dissolved in concentrated sulphuric acid, giving a red solution with orange fluorescence; such properties indicated that no condensation had occurred.

Analysis

| | | | |
|---|---|---|---|
| Found | | C 87.9% | H 3.3% |
| Required for | $C_{28}H_{12}O_2$ | C 88.4% | H 3.2% |
| | $C_{34}H_{20}$ | C 95.4% | H 4.6% |

## SUMMARY

1. The attempted synthesis of 8-phenylmesobenzanthrone by interaction of glycerol and sulphuric acid with
   (a) 1-phenylanthraquinone
   and (b) 1-phenylanthrone
   gave in each case a mixture of sulphonic acids, the desulphonation of which could not be accomplished.

2. A poor yield of a substituted mesobenzanthrone resulted from the condensation of maleic anhydride with 1-phenyl-10-methyleneanthrone. The reaction product was not characterised.

3. Both isoprene and 2:3-dimethylbutadiene undergo diene addition to 2-( $\alpha$ -naphthyl)-acrylic acid. The resulting 2-( $\alpha$ -naphthyl)-tetrahydrobenzoic acids could not be cyclised to mesobenzanthrones. The condensation of 2-( $\alpha$ -naphthyl)-acrylic acid and 1-phenylbutadiene was unable to be effected.

4. 1-(2'-phenylbenzyl) naphthalene, previously obtained in an impure state, has been unequivocally synthesised by two independent routes, involving
   (a) The Friedel-Crafts reaction of naphthalene and o-phenylbenzyl bromide;
   (b) Interaction of $\alpha$ -tetralone with o-phenylbenzylmagnesiumbromide.

5. A possible phenyl group elimination in the aluminium chloride cyclisation of 1-(4'-phenyl-benzoyl)-naphthalene has been shown not to take place, but the resulting 10-phenylmesobenzanthrone could not be completely purified.

6. The condensation of perinaphthanone with aromatic aldehydes has been investigated. An interim suggestion is made that, for benzaldehyde and p. chlorobenzaldehyde, an abnormal product is formed, corresponding to interaction of two molecules of the aldehyde with one molecule of perinaphthanone. When heated with sodium ethoxide, these compounds were degraded to lower melting solids, whose structures were not rigidly established.

7. Attempts to identify the bimolecular hydrocarbon previously obtained in small yield by the phosphorus oxychloride induced self-condensation of mesobenzanthrone have been unsuccessful. Difficulties in the synthesis of four of the possible condensation structures have also been encountered.

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